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GRAVIMETRIC DETERMINATION OF SCANDIUM USING MANDELIC ACID*

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Summary—A new method for the gravimetric determination of scandium using mandelic acid and a method for separating scandium from rare earths and thorium have been developed. The composition of the precipitate corresponds to the formula $H_3[Sc(C_8H_8O_3)_3]\cdot nH_2O$. Thermogravimetric examination of this compound showed that it decomposes at 280°. Scandium mandelate dissolves in ammonia with the formation of $(NH_4)_3[Sc(C_8H_6O_3)_2]_3$.

THE analytical chemistry of scandium has been little studied up to the present.[1] For the determination and separation of this element from other elements inorganic precipitants have been recommended, *e.g.* hydrofluoric acid, fluosilicic acid, pyrophosphoric[2] and hypophosphorous[3] acids, *etc.* Considerably less study has been given to organic precipitants, among which we can mention oxalic acid, 8-hydroxyquinoline[4] and its halogen derivatives[5] and sodium alizarin sulphonate.[6] The most selective precipitant is phytic acid.[7] Scandium can also be precipitated by phenylarsonic acid. A number of colour reactions for scandium are known, among which azo-compounds containing an arsonium group[8] are the most interesting. Lately a method for separating scandium by extraction with organic solvents[9] has been used successfully, as well as a method using ion-exchange chromatography.[10]

On studying the analytical chemical reactions of the scandium ion one finds similar properties to those of the thorium ion and especially those of zirconium and hafnium. The ionic radii of these last two elements are very close to that of scandium. Besides this, the scandium ion, like that of zirconium, has a tendency to polymerisation.[11] This makes it possible to look for new reagents and reactions for scandium using the above similarity and also the difference in the pH of the solution with reactions using organic reagents. Thus, like thorium and zirconium, scandium can be precipitated by derivatives of selenic or telluric acids.[12]

Our investigations have shown that scandium is precipitated in a weakly acid medium by mandelic acid, which is known to be quite a selective reagent for zirconium.[13–18] In the present work the conditions for precipitation of scandium by mandelic acid and the composition of the precipitate have been studied. A method for separating it from rare earth elements and thorium is proposed.

EXPERIMENTAL

Reagents

Standard scandium solution: 0·5 g of spectrally pure scandium oxide were dissolved in 20 ml of concentrated hydrochloric acid with continuous careful heating until all cloudiness had disappeared. The solution obtained was carefully evaporated almost to dryness and the residue dissolved in 500 ml

* Translated from the Russian, *Zhur. analit. Khim.*, 1960, **15**, 1.

of water. The titre of this solution was found by precipitation of the hydroxide with ammonia and weighing as Sc_2O_3.

Precipitation of scandium with mandelic acid

The following procedure was used:

To 35 ml of the standard solution of the scandium salt 15 ml of an 8% solution of mandelic acid were added. After heating in a water bath for 30 min and cooling to room temperature, the white

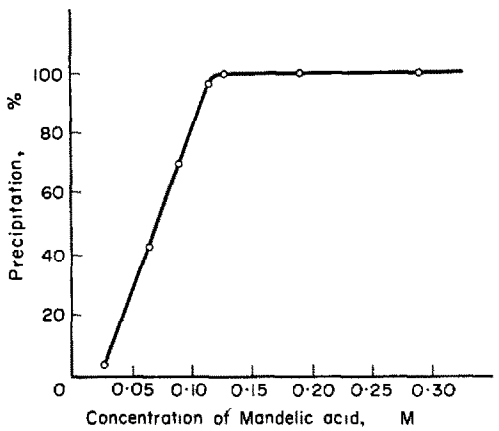


FIG. 1—Effect of concentration of mandelic acid on completeness of scandium precipitation.

flocculent precipitate which separated was washed with a 0·5% solution of mandelic acid, dried and heated at 800° to constant weight.

To find the best conditions for the scandium precipitation the effect of reagent concentration and solution pH were studied. For this purpose, to a solution containing scandium (0·00495 mg of Sc_2O_3) various quantities of 8% mandelic acid solution were added and the precipitate treated as described above. The results of the experiments are shown in Fig. 1.

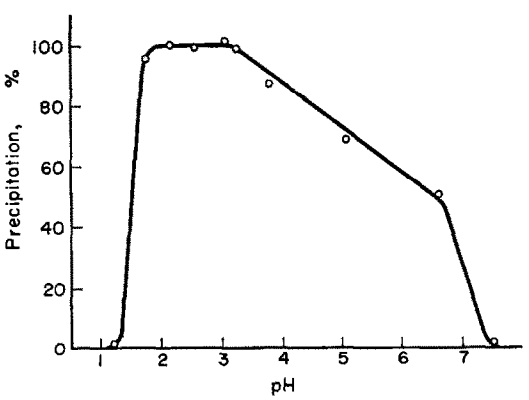


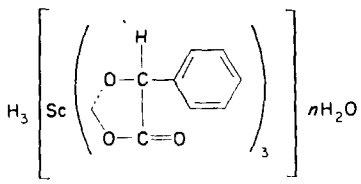
FIG. 2—Effect of pH on completeness of scandium precipitation.

To clarify the dependence of completeness of scandium separation on the pH of the solution, precipitation with mandelic acid at various pH was carried out. The pH was controlled using hydrochloric acid and ammonia. Measurement of the pH of the filtrates was carried out with a glass electrode. The results obtained are given in Fig. 2.

For complete precipitation of the scandium it is necessary to add an excess of reagent and keep the pH of the solution between 1·8–3·2. One should note that zirconium, unlike scandium, precipitates in a solution with 5–7*N* hydrochloric acid. The results from the determination of scandium in solutions of its salts are given in Table I.

Composition and properties of the precipitate

To study the composition of the compound of scandium with mandelic acid the precipitate obtained was filtered off through a glass crucible, washed with 0·5% mandelic acid solution and then, to get rid of the mandelic acid, washed again with ether, in which the precipitate does not dissolve. After this it was dried at 110° and weighed. Part of the precipitate was then heated to constant weight at 800° (about 20–50 mg) and the oxide, Sc_2O_3, weighed. The results (Table II) show that the precipitate separating from a weakly acid medium (pH 2·5) has the composition $H_3[Sc(C_8H_6O_3)]_3 \cdot nH_2O$. This compound, like zirconium mandelate[13,19,20] probably has the following structure:



In the precipitate there is always a trace of coprecipitated mandelic acid and this must be removed by ether washing before weighing. However, more reliable results are obtained by weighing the scandium oxide after calcining the precipitate.

TABLE I—PRECIPITATION OF SCANDIUM BY MANDELIC ACID

Sc_2O_3, *mg*		Error		Sc_2O_3, *mg*		Error	
Taken	Found	*mg*	%	Taken	Found	*mg*	%
9·90	9·92	+0·02	+0·2	4·95	4·90	−0·05	−1·0
9·90	9·90	±0·00	±0·0	4·95	4·98	+0·03	+0·6
4·95	4·95	±0·00	±0·0	0·99	1·02	+0·03	+2·0
4·95	4·94	−0·01	−0·2	0·99	0·98	−0·01	−1·0

TABLE II—ANALYSIS OF THE COMPOUND OF SCANDIUM WITH MANDELIC ACID

Weight of precipitate, *mg*	Found, *mg*		Molar ratio of Sc:$C_8H_7O_3$
	Sc	$C_8H_7O_3$	
24·5	2·2	22·3	1:3·0
34·1	3·0	31·1	1:3·1
55·7	4·9	50·8	1:3·1
55·1	4·9	50·2	1:3·0

The thermogravigram (Fig. 3) obtained from constant weighing shows that the compound is stable up to 280° and decomposes at higher temperatures. In the range 340–390° an intermediate compound is formed which is transformed to scandium oxide at 500°.

The scandium precipitate, like the analogous zirconium[21] and hafnium[22] compounds, dissolves

easily in ammonia. The composition of this compound was studied by Hahn's method,[22] which was applied for the study of the analogous compound of hafnium.

A measured amount of the precipitate, obtained as described above, was dissolved in an excess of standard 0·092*N* solution of ammonia, after which the excess ammonia was titrated with 0·1*N* hydrochloric acid using a glass electrode. The results of the determinations are given in Table III and Fig. 4 and indicate that the reaction for the solution of the precipitate in ammonia follows the equation:

$$H_3[Sc(C_8H_6O_3)_3] + 3NH_4OH \rightleftharpoons (NH_4)_3[Sc(C_8H_6O_3)_3] + 3H_2O.$$

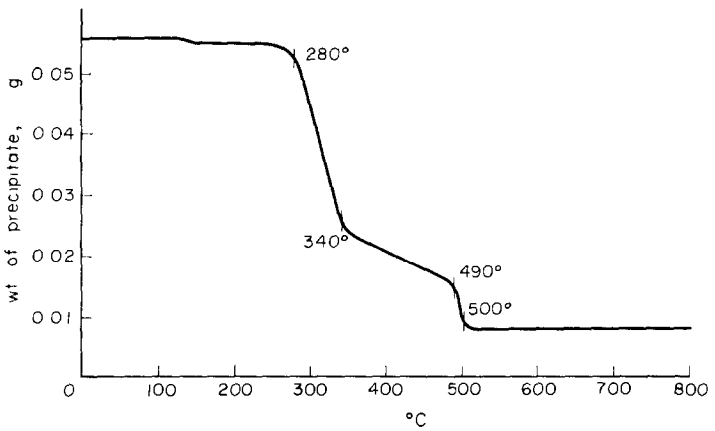


FIG. 3—Thermogravigram of precipitate of $H_3[Sc(C_8H_6O_3)_3]\cdot nH_2O$. Weight of precipitate in g.

TABLE III—DETERMINATION OF THE COMPOSITION OF THE PRECIPITATE AFTER DISSOLVING IN AMMONIA

Weight of precipitate, *mg*	Mean volume of NH_4OH, *ml*	Volume of HCl solution, *ml*	Excess NH_4OH, *ml*	NH_4OH to dissolve precipitate, *ml*	Ratio of $NH_4OH:H_3[Sc(C_8H_6O_3)_3]$
71·6	25·0	18·4	20·2	4·8	3·1:1
105·5	25·0	16·6	18·2	6·8	3·0:1
150·4	25·0	13·6	14·9	10·1	3·1:1
175·0	25·0	12·5	13·7	11·3	3·0:1
226·2	25·0	9·5	10·4	14·6	2·9:1

The precipitate is also soluble in organic solvents such as pyridine and ethylenediamine. The action of sodium hydroxide forms the hydroxide of scandium. From the titration curve (Fig. 4) it can clearly be seen that the precipitate is soluble in ammonia at a pH above 6.3.

Separation of scandium from the rare earth elements and thorium

The rare earth elements and thorium do not give a precipitate with mandelic acid at pH 2–3 and hence they can be separated from the scandium. For this purpose titrated solutions of the nitrates of the rare earths and thorium were used. The precipitation was carried out as described above. For quantitative separation of the rare earth elements the scandium had to be reprecipitated. For this the good solubility of the precipitate in concentrated ammonia was used. The ammonia was added in drops on to the filter. After washing the filter with distilled water the solution was neutralised with 4*N* hydrochloric acid to an acid reaction with methyl orange, and 15 ml of 8% mandelic acid solution added. The solution was then heated on a water bath for 30 min and, after cooling, the precipitate was filtered off through the same filter.

The results of the determination of scandium in the presence of rare earth elements are given in Table IV.

The separation of scandium from thorium was carried out in the same way. One should note that large quantities of thorium interfere in the scandium determination.

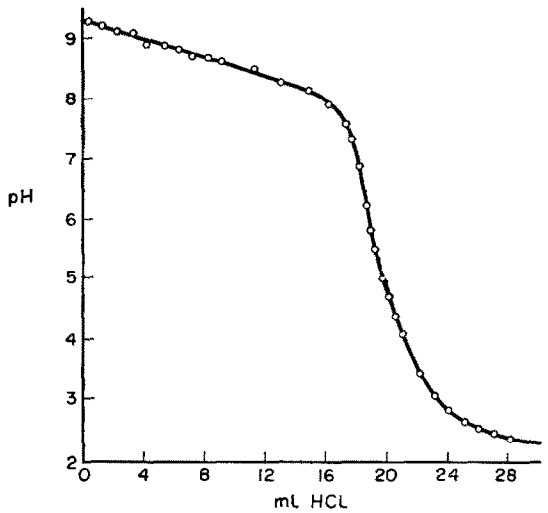


FIG. 4.—Potentiometric titration of ammoniacal solution of scandium mandelate with hydrochloric acid.

TABLE IV—DETERMINATION OF SCANDIUM IN THE PRESENCE OF RARE EARTH ELEMENTS

Ratio of Sc:R.E. elements	Sc_2O_3, *mg*		Error		No. of precipitations
	Taken	Found	*mg*	%	
1:1	2·97	3·12	+0·15	+5·0	1
	2·97	3·13	+0·16	+5·3	
	2·97	2·97	±0·00	±0·0	2
	2·97	3·01	+0·04	+1·3	
	2·97	2·95	−0·02	−0·7	
1:5	2·97	3·15	+0·18	+6·0	2
	2·97	3·10	+0·13	+4·3	
	2·97	3·04	+0·07	+2·3	3
	2·97	2·93	−0·04	−1·3	
1:10	2·97	2·96	−0·01	−0·3	3
	2·97	3·03	+0·06	+2·0	

If the pH is increased coprecipitation of thorium takes place. Complexing the thorium with organic acids such as trioxyglutaric or lactic acids was tried, but it appeared that the scandium is also masked by these acids and gives no precipitate. The results of the separation of scandium from thorium are given in Table V.

TABLE V—DETERMINATION OF SCANDIUM IN THE PRESENCE OF THORIUM
(ratio of Sc:Th = 1:1)

Sc_2O_3, *mg*		Error		Number of precipitations
Taken	Found	mg	%	
4·95	4·97	+0·02	+0·4	1
4·95	5·05	+0·10	+2·0	1
2·97	3·02	+0·05	+1·8	1
2·97	3·00	+0·03	+1·0	2

CONCLUSIONS

A new method has been developed for the determination of scandium using mandelic acid, as well as a method for the separation of scandium from the rare earth elements and thorium. The precipitate composition corresponds to the formula $H_3[Sc(C_8H_6O_3)_3]\cdot nH_2O$. This compound, as was shown by the thermogravigram, decomposes at 280°. Scandium mandelate dissolves in ammonia with the formation of $(NH_4)_3Sc(C_8H_6O_3)_3$.

Zusammenfassung—Neue Methoden zur gravimetrischen Bestimmung von Scandium mit Mandelsäure und zu dessen Abtrennung von den seltenen Erden werden beschrieben. Die Zusammensetzung des Niederschlages ist $H_3[Sc(C_8H_6O_3)_3]\cdot nH_2O$ Thermogravimetrische Untersuchung der Verbindung zeigt Zersetzung bei 280°C. Scanidiummandelat löst sich in Ammoniak unter Bildung von $(NH_4)_3[Sc(C_8H_6O_3)_3]$.

Résumé—Les auteurs ont mis au point une nouvelle méthode de dosage gravimétrique du scandium utilisant l'acide mandélique, et une méthode de séparation du scandium des terres rares et du thorium. La composition du précipité correspond à la formule $H_3[Sc(C_8H_6O_3)_3]\cdot nH_2O$. L'étude thermogravimétrique de ce composé montre qu'il se décompose à 280°. Le mandélate de scandium se dissout dans l'ammoniaque avec formation de $(NH_4)_3[Sc(C_8H_6O_3)_3]$.

REFERENCES

[1] *Scandium.* Translations edited by L. N. Komissarova, Izd. vo inostran. lit. M., 1958.
[2] G. Beck, *Mikrochem. Mikrochim. Acta*, 1951, **37**, 790.
[3] D. R. Bomberger, *Analyt. Chem.*, 1958, **30**, 1907.
[4] L. Pokras and H. R. Bernays, *ibid.*, 1951, **23**, 757.
[5] T. Moeller and M. V. Ramaniah, *J. Amer. Chem. Soc.*, 1954, **76**, 6030.
[6] G. Beck, *Mikrochim. Acta*, 1937, **2**, 9.
[7] *Idem, Mikrochem. Mikrochim. Acta*, 1948, **34**, 62, 282.
[8] V. I. Kuznetsov, *Zhur. Obshchei. Khim.*, 1944, **14**, 897.
[9] G. H. Morrison and H. Freiser, *Solvent Extraction in Analytical Chemistry.* Wiley, New York, 1957.
[10] E. Lederer and M. Lederer, *Chromatography.* Elsevier, Amsterdam, 1953.
[11] L. Pokras, *J. Chem. Educ.*, 1956, **33**, 16, 284.
[12] I. P. Alimarin and V. S. Sotnikov, *Vestnik Mosk. Univ.*, 1957, (6), 137.
[13] C. A. Kumins, *Analyt. Chem.*, 1947, **19**, 376.
[14] A. A. Astanina and E. A. Ostroumov, *Zhur. Analit. Khim.*, 1951, **6**, 27.
[15] M. Venkataramaniah and Bh. S. V. R. Rao, *J. Indian Chem. Soc.*, 1951, **28**, 257.
[16] R. Belcher, A. Sykes and J. C. Tatlow, *Analyt. chim. Acta*, 1954, **10**, 34.
[17] R. B. Hahn and L. Weber, *Analyt. Chem.*, 1956, **28**, 414.

[18] V. M. Peshkova, N. V. Mel'chakova and A. B. Urazekova, *Vestnik Mosk. Univ.*, 1959, (6), 150.
[19] R. E. Oesper and I. I. Klingenburg, *Analyt. Chem.*, 1949, **21**, 1509.
[20] F. Feigl, *Chemistry of Specific, Selective and Sensitive Reactions*. Academic Press, New York, 1949, 213.
[21] R. B. Hahn and L. Weber, *J. Amer. Chem. Soc.*, 1955, **77**, 4777.
[22] R. B. Hahn and P. I. Joseph, *ibid.*, 1957, **79**, 1298.

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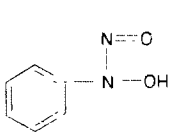
DETERMINATION OF ZIRCONIUM USING *N*-BENZOYLPHENYLHYDROXYLAMINE*

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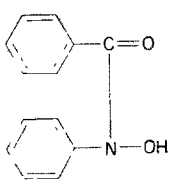
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Summary—A new method has been developed for the quantitative precipitation of zirconium with *N*-benzoylphenylhydroxylamine. The influence of different mineral acids, tartaric acid and hydrogen peroxide on the completeness of the precipitation has been studied. Precipitation of zirconium in the presence of other elements has been investigated. It has been shown that zirconium can be separated from iron, aluminium, chromium, titanium, niobium and tantalum. The composition of zirconium benzoylphenylhydroxylaminate has been determined. The precipitate separated from a strong acid solution corresponds to the formula $Zr(BPHA)_4$.

ORGANIC reagents, such as cupferron[1–6] and its analogue *N*-benzoylphenylhydroxylamine (BPHA), have recently been widely used for the determination of zirconium and its separation from other elements. BPHA was recommended as an analytical reagent for precipitation of metals by Bamberger.[7]



Cupferron



N-Benzoylphenylhydroxylamine

Shome[8–10] used BPHA for determining titanium, aluminium and copper gravimetrically and vanadium photometrically. He showed that BPHA differs from cupferron in its stability to the action of light and heat. Ryan and Lutwik[11] used BPHA for determining tin. Moshier and Schwarberg[12] and Majumdar and Mukherjee[13] used this reagent for determining titanium. Sinha[14] applied BFHA to the determination of molybdenum and Dyrssen[15] to the extraction of lanthanum, thorium and uranium.

The aim of the present work was to find more precisely the conditions needed for determining zirconium using *N*-benzoylphenylhydroxylamine, both in pure salts and in the presence of other elements, and also to attempt the separation of zirconium from tantalum and several other elements by this means.

EXPERIMENTAL

The *N*-benzoylphenylhydroxylamine was synthesised by Shome's method.[8] The product was recrystallised from ethyl alcohol (or hot water). This reagent consists of white needle-like crystals (m.p. 121°), sparingly soluble in cold water [at room temp. (25°) about 0·5 g/l.] and easily soluble in hot water, alkali solutions, ethyl alcohol, diethyl ether, chloroform and cyclohexanone. The reagent is quite stable in sulphuric or hydrochloric acid solution; only in strongly alkaline solutions can some decomposition be observed after a few days.

For these experiments a solution of zirconium oxychloride was used, the concentration of the solution being found gravimetrically.

* Translated from the Russian: *Zhur. analit. Khim.*, 1959, **14**, 5.

To determine the best conditions for the precipitation of zirconium by BPHA the relationship between the completeness of zirconium precipitation and the quantity of BPHA was studied. For this, various amounts of BPHA, dissolved in 40 ml of boiling water (mean volume 100 ml; hydrochloric acid concentration 0·15*N*), were added to 60 ml of a standard zirconium solution (0·0152 g of ZrO_2). The solution and precipitate were heated on a boiling water bath for 10–15 min with occasional stirring. In this way the zirconium benzoylphenylhydroxylaminate was separated as a white, well coagulated precipitate. On cooling, the precipitate was filtered off through a fine filter, washed with 0·1% hydrochloric acid solution containing 0·05% BPHA, dried and heated in a porcelain crucible at 1000–1100° to constant weight. The results obtained are shown in Fig. 1.

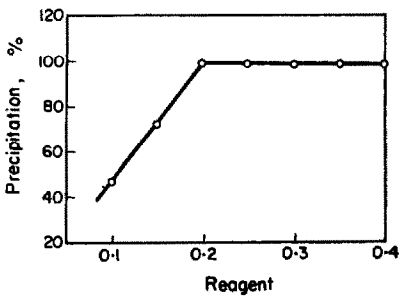


FIG. 1.—Dependence of completeness of precipitation of zirconium on the quantity of BPHA. (Weight in g)

One should note that, for practical purposes, it is as well to add an excess of reagent for complete precipitation, especially in a strongly acid medium.

To clarify the influence of acidity on the completeness of precipitation, zirconium precipitation by BPHA was carried out in various acid concentrations in the solution. The results are given in Fig. 2.

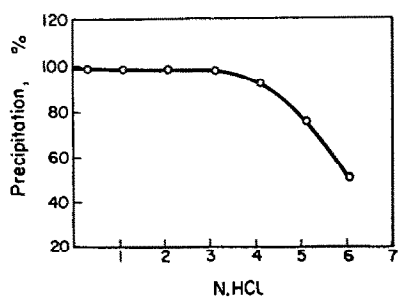


FIG. 2.—Effect of hydrochloric acid concentration on completeness of precipitation of zirconium by BPHA.

The effect of various mineral acids and tartaric acid on the zirconium precipitation was then studied. For this purpose, to a solution containing zirconium various amounts of hydrochloric, sulphuric or tartaric acids were added, the solution diluted to 150 ml, then 0·4–0·5 g of BPHA, dissolved in 100 ml of boiling water, added. The solution and precipitate were heated for 15–20 min on a boiling water bath with occasional stirring. The precipitate was immediately filtered off through a fine filter, because the BPHA-zirconium compound is practically insoluble in boiling water. The precipitate was washed with 1·0% hydrochloric acid solution containing 0·05% BPHA, dried and heated in a porcelain crucible at 1000–1100° to constant weight. The results obtained are shown in Table I.

To clarify the effect of the hydrogen peroxide, used for preventing titanium, niobium, tantalum and vanadium precipitation, on the completeness of zirconium precipitation, to 150 ml of solution containing zirconium about 1 ml of 30% hydrogen peroxide was added, then precipitation by BPHA carried out as described above. The precipitate was filtered off, calcined and weighed. The results of the experiments, given in Table I, show that hydrogen peroxide has no effect on the completeness of

TABLE I

ZrO_2, *g*		Error, *g*	Medium
Taken	Found		
0·0303	0·0303	±0·0000	2·4*N* HCl
0·0303	0·0304	+0·0001	
0·0152	0·0151	−0·0001	
0·0152	0·0153	+0·0001	
0·0062	0·0062	±0·0000	
0·0062	0·0062	±0·0000	
0·0062	0·0062	±0·0000	
0·0016	0·0016	±0·0000	
0·0016	0·0017	+0·0001	
0·0031	0·0031	±0·0000	2·4*N* HCl and 5% $C_4H_6O_6$
0·0031	0·0030	−0·0001	
0·0031	0·0031	+0·0000	2·4*N* HCl and 0·15% H_2O_2
0·0031	0·0033	+0·0002	
0·0152	0·0151	−0·0001	2·4*N* HCl (95°)
0·0152	0·0150	−0·0002	
0·0152	0·0153	+0·0001	3·6*N* H_2SO_4
0·0062	0·0064	+0·0002	
0·0152	0·0154	+0·0002	3·6*N* H_2SO_4 and 5% $C_4H_6O_6$
0·0062	0·0062	±0·0000	
0·0152	0·0152	±0·0000	3·6*N* H_2SO_4 and 0·15% H_2O_2
0·0062	0·0062	±0·0000	

zirconium precipitation. One should note that, in the presence of the hydrogen peroxide, the solution and precipitate are best heated on a weakly boiling water bath for not more than 15 min.

Zirconium precipitation in the presence of other elements was studied next. Standardised solutions of salts of iron, aluminium, chromium, titanium, niobium, tantalum and the rare earth elements were used. Precipitation and determination of zirconium were carried out as described above. The results of these experiments are given in Table II.

In the precipitates obtained only traces of iron were present; none of the other elements were found.

TABLE II*

Oxides of other metals added, *g*	ZrO_2 found, *g*	Error, *g*	Oxides of other metals added, *g*	ZrO_2 found, *g*	Error, *g*
Fe_2O_3 0·033	0·0032	+0·0001	Cr_2O_3 0·20	0·0031	±0·0000
Fe_2O_3 0·033	0·0031	±0·0000	Cr_2O_3 0·020	0·0031	±0·0000
Al_2O_3 0·150	0·0033	+0·0002	Cr_2O_3 0·010	0·0030	−0·0001
Al_2O_3 0·150	0·0030	−0·0001	Cr_2O_3 0·020	0·0029	−0·0002
TiO_2 0·018	0·0031	±0·0000	$(Nb, Ta)_2O_5$ 0·010	0·0030	−0·0001
TiO_2 0·018	0·0033	+0·0002	$(Nb, Ta)_2O_5$ 0·010	0·0030	−0·0001

* 0.0031 g of ZrO_2 taken.

The precipitate of zirconium benzoylphenylhydroxylaminate used for determining its composition was prepared as follows: To a solution containing zirconium various quantities of hydrochloric acid and 0·5–1·5 g of BPHA dissolved in 50–100 ml of boiling water (mean volume 100–150 ml) were added. The solution and precipitate were heated on a boiling water bath for 30 min and, without cooling, the precipitate was filtered off through a glass crucible and washed with hot 1% hydrochloric acid solution containing 0·05% BPHA and several times with boiling distilled water. The precipitate was then washed with 30 ml of ether (BPHA dissolves in ether while the zirconium compound does not) and dried at 105–110° to constant weight. Weighed portions of the precipitate were transferred to a porcelain crucible, heated at 1000–1100° to constant weight and weighed as ZrO_2. The results obtained are given in Table III and show that the composition of the precipitate separating from hydrochloric acid solution corresponds to the formula $Zr(BPHA)_4$.

TABLE III

Weight of ppt. of zirconium benzoylphenylhydroxylaminate, *g*	Found, *g*		Zr:BPHA	HCl Concn., *N*
	Zr	BPHA (by difference)		
0·1170	0·0119	0·1051	1:3·8	0·15
0·1168	0·0119	0·1049	1:3·8	0·15
0·1170	0·0119	0·1051	1:3·8	1·0
0·1150	0·0119	0·1031	1:3·7	1·0
0·1169	0·0119	0·1050	1:3·8	2·3
0·0554	0·0053	0·0501	1:4·0	3·1
0·0951	0·0091	0·0860	1:4·0	4·2
0·0940	0·0093	0·0847	1:4·0	5·3
0·0958	0·0094	0·0864	1:4·0	6·0

The $Zr(BPHA)_4$ compound can itself be used as a weighing form.

To find the stability of the compound to temperature a thermogravimetric analysis was carried out. From Fig. 3 it can be seen that the precipitate is stable up to 240°. To obtain ZrO_2 it is sufficient to heat the precipitate to 500°.

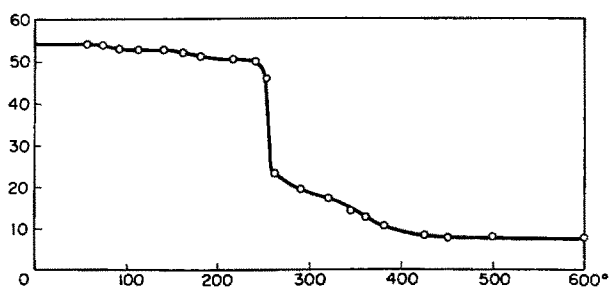


FIG. 3.—Thermoanalysis curve for zirconium benzoylphenylhydroxylaminate (Weight in mg).

CONCLUSIONS

A new method has been developed for the quantitative precipitation of zirconium with *N*-benzoylphenylhydroxylamine. The influence of different mineral acids, tartaric acid and hydrogen peroxide on the completeness of the zirconium precipitation with N-benzoylphenylhydroxylamine has been studied. Precipitation of zirconium in the presence of other elements has been investigated. It has been shown that zirconium can be separated from iron, aluminium, chromium, titanium, niobium

and tantalum. The composition of zirconium benzoylphenylhydroxylaminate has been determined; the precipitate separated from a strong acid solution corresponds to the formula $Zr(BPHA)_4$.

Zusammenfassung—Eine neue Methode zur quantitativen Fällung von Zirkonium mit N-benzoylphenylhydroxylamin wurde entwickelt. Der Einfluss verschiedener Mineralsäuren, sowie von Tartrat und Wasserstoffperoxyd auf die Vollständigkeit der Fällung wurde studiert. Die Fällung von Zirkonium in Gegenwart anderer Elemente wurde untersucht. Es wurde gezeigt, dass Zirkonium von Eisen, Aluminium, Chrom, Titan, Niob und Tantal getrennt werden kann. Die Zusammensatzung des Niederschlages wurde ermittelt: Zr: organischer Rest = 1:4, wenn aus stark saurem Medium gefällt wird.

Résumé—Les auteurs ont mis au point une nouvelle méthode de précipitation quantitative du zirconium par la N-benzylphénylhydroxylamine. L'influence de différents acides minéraux, de l'acide tartrique et de l'eau oxygénée sur la totalité de la précipitation a été étudiée. La précipitation du zirconium en présence d'autres éléments a été examinée. Les auteurs ont montré que le zirconium peut être séparé du fer, de l'aluminium, du chrome, du titane, du niobium et du tantale. La composition du benzylphénylhydroxylaminate de zirconium a été déterminée; le précipité séparé en solution fortement acide correspond à la formule $Zr(BPHA)_4$.

REFERENCES

[1] O. Baudisch, *Chem.-Ztg.*, 1909, **33,** 1298; *Ber.*, 1916, **49,** 172; *Arch. Kemi. Mineral Geol.*, 1938, **12B** (8).
[2] W. M. Thornton and E. M. Hayden, *Amer. J. Sci.*, 1941, **38,** 137.
[3] G. F. Smith, *Cupferron and Neocupferron.* G. F. Smith Chem. Co. Columbus, 1938.
[4] N. Furman, W. B. Mason and J. S. Pekola, *Analyt. Chem.*, 1949, **21,** 1325.
[5] E. C. Olson and P. J. Elving, *ibid.*, 1954, **26,** 1747.
[6] Yu. I. Usatenko and G. E. Bekleshova, *Zavodskaya Lab.*, 1957, **23,** 1406.
[7] E. Bamberger, *Ber.*, 1919, **52,** 1116.
[8] S. C. Shome, *Analyst*, 1950, **75,** 27.
[9] *Idem, Analyt. Chem.*, 1951, **23,** 1186.
[10] *Idem, Current Sci.*, 1944, **13,** 257.
[11] D. E. Ryan and G. D. Lutwik, *Canad. J. Chem.*, 1953, **31,** 9.
[12] R. W. Moshier and J. E. Schwarberg, *Analyt. Chem.*, 1957, **29,** 947.
[13] A. K. Majumdar and A. K. Mukherjee, *Naturwiss.*, 1957, **44,** 491.
[14] S. K. Sinha and S. C. Shome, *Current Sci.*, 1957, **26,** 249.
[15] D. Dyrssen, *Acta Chem. Scand.*, 1956, **10,** 353.

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SPECTROPHOTOMETRIC DETERMINATION OF RHODIUM AFTER OXIDATION WITH HYPOBROMITE

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Summary—In the presence of hypobromite at pH ~ 11, rhodium yields a violet colour, with a maximum at 530 mμ, suitable for the quantitative determination of 10–60 ppm of Rh in the presence of platinum. The solution turns blue on standing or on adding a reducing agent; a green colour is obtained at pH < 10 and a yellow one at low BrO^- concentration. Evidence is given for Rh^{VI} in the violet solutions and Rh^V in the blue solutions. The disproportioning: $3\ Rh^V \rightleftarrows 2\ Rh^{VI} + Rh^{III}$ proceeds in the forward direction in acidic medium.

VERY few references to the oxidation of rhodium solutions to a valency state higher than +3 are found in the literature. A mixture of oxidation states, the +6 being quite evident, was obtained by Grube *et al.*[1] by the electrolytic oxidation of sulphuric or perchloric acid solutions. Syrokomsky and Proshenkova[2] obtained violet Rh^V by treating a rhodium solution in sulphuric acid with sodium bismuthate. Ayres and Young[3] found that a blue colour is developed in the presence of an excess of hypochlorite in buffered solutions. This colour is suitable for the spectrophotometric determination of rhodium, and it can be attributed to the formation of Rh^V. A difference between buffered (blue) and acidic (purple) solutions seems to result from different forms,[4] anionic and cationic, respectively, of the same oxidation state.

The possibility of rhodium oxidation in strongly alkaline medium has not yet been fully investigated. In the present paper, which follows previous work on the chemistry of rhodium,[5–8] such a medium is taken into account; as a reagent, sodium hypobromite, whose reaction with rhodium has not previously been examined, is employed.

EXPERIMENTAL

Apparatus

The absorption curves were obtained with a Beckman DU spectrophotometer; a Metrohm E 148 c potentiometer was used for the measurement of pH.

Reagents

A standard 0·02*M* Rh solution was prepared from $Na_3RhCl_6.2H_2O$. Sodium hypobromite was prepared by dissolving 100 g of pure Br_2 in 200 ml of 6*N* NaOH, adding further NaOH to give a pH of 11·2 (potentiometrically controlled), and diluting the solution to 500 ml; the reagent was standardised iodometrically.

RESULTS

A violet colour is developed in a rhodium^{III} solution with an excess of hypobromite at room temperature. The stability of this colour depends on the hypobromite concentration: the solution remains violet for several days with 1 *M* hypobromite, but turns blue within a few hours when the reagent is 0·1*M*; the variation in the absorption spectrum on standing is shown in Fig. 1. The violet species shows a maximum at 530 mμ, suitable for the spectrophotometric determination of rhodium. An extensive investigation of the factors which affect the spectrophotometric results was therefore carried out.

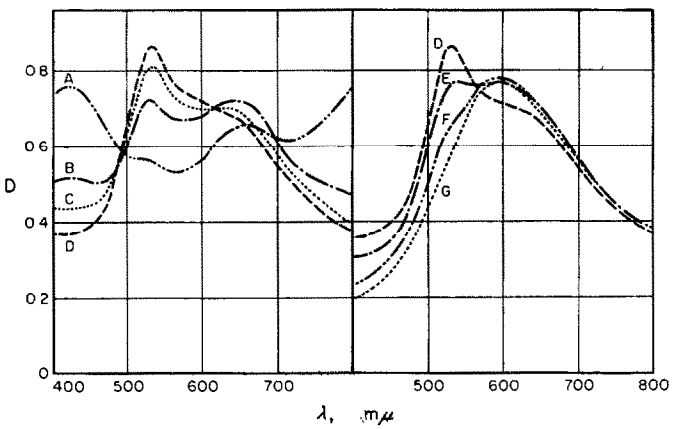


FIG. 1.—Ageing of 0·85*mM* Rh in 0·12*M* BrO^-.
Left side: formation of the violet colour; right side: formation of the blue colour.
Spectra are registered after (A) 5 min, (B) 15 min, (C) 25 min, (D) 40 min, (E) 1·5 hr, (F) 2·5 hr, (G) 5·5 hr.

Influence of pH

The alkalinity of the medium must be controlled with accuracy, if reproducible results are to be obtained. Although at pH > 10 a violet colour is always obtained, the strongest absorption is found at pH 11·2–11·3. The plot of optical density at 530 mμ *vs.* pH is shown in Fig. 2.

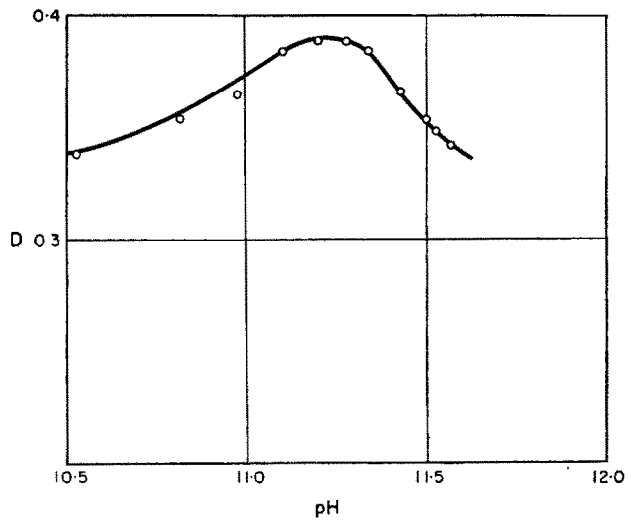


FIG. 2.—Variation of the absorbance at 530 mμ with pH.
0·3*mM* Rh in 0·6*M* BrO^-.

Rhodium concentration

With varying rhodium concentration, Beer's law is obeyed if measurements are carried out after stabilisation for 0·5–1 hour. The optimum analytical range is 10–60 ppm of rhodium. The molar extinction coefficient at 530 mμ is 1270 in 0·3*M* hypobromite.

Reagent concentration

Using varying amounts of hypobromite, variation in the absorbance measurements may be expected in accordance with the plot in Fig. 3A. However, if the concentration of hypobromite is greater than 0·2*M*, no rigorous control is necessary, the variation of the spectrum with the concentration of hypobromite being very small.

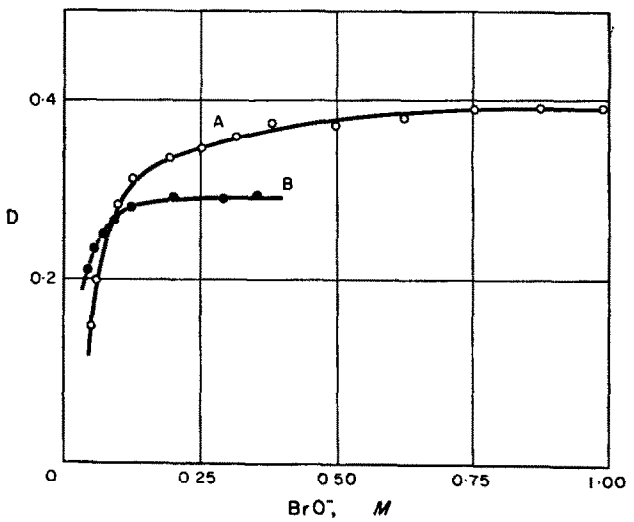


FIG. 3.—Variation in the absorbance of 0·3*mM* Rh with [BrO^-].
A: violet solutions, $\lambda = 530$ mμ.
B: blue solutions, $\lambda = 590$ mμ.

Interference of anions

According to the results in Table I, the presence of the anions which are commonly

TABLE I.—PERMISSIBLE SALT CONCENTRATION IN SPECTROPHOTOMETRIC DETERMINATION OF RHODIUM

Salt	Limiting concentration, *moles/litre*	
	Violet solutions $\lambda = 530$ mμ	Blue solutions $\lambda = 590$ mμ
KCl	1	1·5
$NaNO_3$	0·8	1
K_2HPO_4	0·2	0·15
K_2SO_4	0·2	0·4
KBr	1	*

* The formation of the blue colour is progressively delayed with increase in bromide concentration.

encountered affects the rhodium-hypobromite reaction very little. A solution containing a relatively high amount of sulphate or phosphate ions can be used; no interference is found in practice in the presence of chloride or nitrate, and therefore the spectrophotometric determination can be performed on solutions obtained by treatment of the sample with *aqua regia*.

Presence of noble metals

The main interference in the determination of rhodium might be expected to be caused by the presence of platinum metals. A marked alteration is in fact found in the spectrum when iridium or ruthenium are present, while a lesser interference is produced by palladium, osmium or platinum. In Table II the amount of interfering ion which produces a variation of less than 0·01 in optical density is indicated.

TABLE II.—PERMISSIBLE AMOUNTS OF PLATINUM METALS IN SPECTROPHOTOMETRIC DETERMINATION OF RHODIUM

Element	Limiting concentration, *ppm*	
	Violet solutions $\lambda = 530$ mμ	Blue solutions $\lambda = 590$ mμ
Iridium	2	1
Osmium	50	80
Palladium	13	7
Platinum	260	400
Ruthenium	1	2

Because of the slight interference from platinum, it is possible to determine rhodium in the presence of appreciable amounts of platinum, of the order found in the platinum-rhodium alloys used for thermocouples. The absorption of Pt^{IV} at 530 mμ is not, however, negligible for a Pt : Rh ratio greater than 10 : 1. In such a case it is convenient to perform all measurements, including the calibration curve, at 540 mμ; at this wavelength the absorption of rhodium is only a little lower than at 530 mμ,

TABLE III.—DETERMINATION OF RHODIUM IN THE PRESENCE OF PLATINUM.
(Measurements on 10 ml, 0·3*M* in BrO^-, violet colour, after 1 hr.)

Taken, *mg*		D 540 mμ	Rh found, *mg*
Rh	Pt		
0·165	1·05	0·182	0·167
0·165	2·38	0·186	0·171
0·165	3·43	0·184	0·169
0·288	1·32	0·310	0·287
0·288	2·64	0·314	0·290
0·288	4·22	0·306	0·284
0·329	3·70	0·363	0·335
0·329	4·75	0·357	0·329
0·329	5·28	0·365	0·337

while that of platinum is practically negligible. In this way it was found possible to determine rhodium with a Pt : Rh ratio higher than 20 : 1, as shown by the results in Table III.

Analytical procedure

The spectrophotometric determination can be performed in the following way. From the sample solution, which generally is an acidic one, take a volume corresponding to 0·1–1 mg of Rh. Add NaOH solution dropwise to neutralisation point. Add 10 ml of hypobromite reagent, and dilute to 25 ml in a volumetric flask. After a 1-hour interval to stabilise the violet colour, measure the absorbance at 530 mμ and compare with a calibration curve obtained under the same conditions.

Blue solutions

As indicated in Fig. 1, the violet solutions on standing turn blue at any pH higher than 10. This change occurs more slowly with higher hypobromite concentration and lower rhodium concentration. The stability of the violet solutions is also affected by bromide concentration: with 3*M* bromide the violet colour can still be observed after four days. An absorption maximum is found at 590 mμ in the blue solutions, quite different from the one at 665 mμ observed in the blue solutions reported by Ayres and Young;[3] taking into account the difference in pH, it is reasonable to attribute the two such colours, similar in appearance although they may be, to two different ionic forms.

With low rhodium concentrations, the absorbance at 590 mμ follows Beer's law, the molecular extinction coefficient being 920; for higher values a blue-black precipitate is obtained on ageing. This phenomenon prevents the use of the blue colour for analytical purposes. The influence of the variation in hypobromite concentration is shown in Fig. 3B; in Tables I and II the effect of the presence of both foreign anions

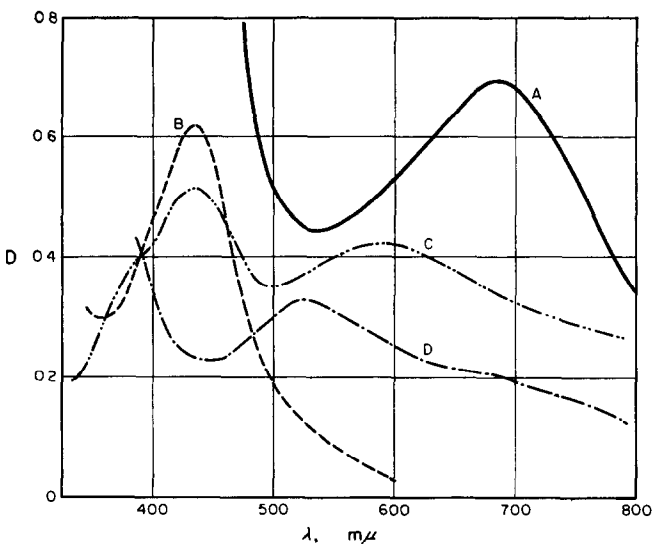


FIG. 4.—A: 0·4*mM* Rh in 0·2*M* BrO^- + CH_3COOH up to pH 8·3 (green).
B: 1*mM* Rh + 6*mM* BrO^- (yellow).
C: 0·7*mM* Rh + 12*mM* BrO^- (green).
D: 0·65*mM* Rh in 0·12*M* BrO^- (violet colour, by adding CH_3COOH up to pH 5·3 to a blue solution).

and foreign cations is shown. The values are practically the same as for the violet solutions.

Green solutions

When the reaction with hypobromite takes place at pH < 10, a green colour is obtained instead of a violet one. A maximum occurs at 690 mμ in the spectrum (Fig. 4A); it does not seem that this colour can be a sum of blue and yellow. Because of the very low stability of the colour, it is of no value for colorimetric determination.

Yellow solutions

With a concentration of hypobromite in the same range as that of rhodium, a yellow colour appears at the same pH as for the violet solutions, with an absorption maximum at 435 mμ (Fig. 4B). With a slight increase in the reagent concentration a green solution is obtained; this colour, however, is quite different from that produced at pH < 10; two maxima are now evident (Fig. 4C), and this colour can be attributed to a sum of the yellow and blue products. It is not easy to determine the reagent ratio in the rhodium-hypobromite reaction; an attempt was made to do this in the yellow solutions by employing Job's method: from Fig. 5 a ratio between 1 : 3 and 1 : 4 is indicated. Such a value leads to the conclusion that an excess of the reagent is necessary to obtain the yellow colour.

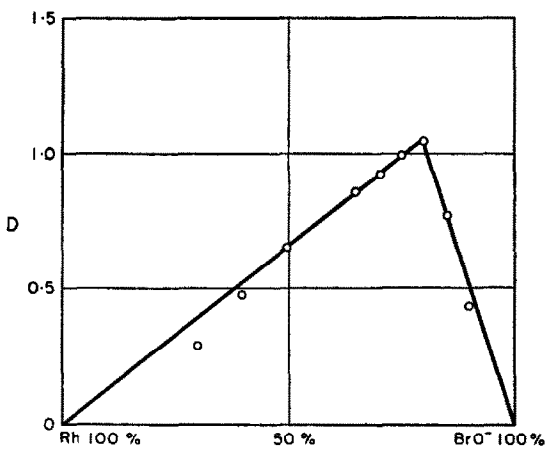


FIG. 5.—Absorbance at 435 mμ versus the rhodium:hypobromite ratio (Rh + BrO^- = 2mM).

CONCLUSIONS

Nature of the species in solution

On adding H^+ to the blue solutions to produce a pH of 5–6, a violet colour is again observed (spectrum in Fig. 4D), practically identical to the colour from which the blue solutions were originally derived. For absorbance, however, particularly at the maximum at 530 mμ, values exactly two-thirds of those observed on the first violet colour, with the same amount of rhodium, were obtained. At this pH value it was feasible to absorb the violet solutions by a cation-exchange resin. After washing the resin, it is possible to elute with 2N HCl, and the eluted solution shows the same violet colour. On adding OH^- to give a pH of 10–11, the blue colour is restored: the colour change is completely reversible with variation in pH. Iodometric titrations were carried out on the eluted violet solutions: the redox equivalents found for 4·1, 8·2, 10·3, 12·4 and 14·5 mg of Rh, were respectively 2·24, 2·12, 2·07, 2·15 and 2·04.

It would appear possible that the rhodium may be present in the +5 oxidation state, but other phenomena have to be taken into account.

The blue colour, with its absorption maximum at 590 mμ, can be obtained from the violet alkaline solutions not only by ageing, but also by adding a reducing agent. Moderate amounts of hypophosphite, sulphite, thiosulphate, formate or thiourea were used successfully: the blue colour was obtained in each case, with a sufficiently reproducible absorbance. In addition, the violet colour in alkaline medium can be restored, with a quantitatively identical absorbance, by adding a moderate excess of hypobromite to the blue solutions: on the whole, some oxidation-reduction phenomena must clearly be involved in the colour change.

On the basis of the above mentioned iodometric titrations, the +5 oxidation state can be ascribed to rhodium in the blue solutions*; consequently the violet colour in alkaline medium should correspond to a valency state +6. The appearance of the violet colour on acidification of the blue solutions could be explained by assuming that rhodium^{V} is not stable in acid medium and undergoes a disproportioning according to the schematic reaction:

$$3\ Rh^{V} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} 2\ Rh^{VI} + Rh^{III}.$$

This would agree with the experimental observation that the spectrum of the violet solution obtained on acidification of the blue solution shows only two-thirds of the absorbance appropriate to the actual total rhodium concentration.

Zusammenfassung—In Gegenwart von Hypobromit bei pH 11 gibt Rodium eine violette Färbung, (Maximum bei 530 mμ), die geeinget ist, dieses Element im Bereich von 10 bis 60 ppm zu bestimmen Die Bestimmung kann auch in Gegenwart von Platin erfolgen. Die Lösung wird blau, wenn stehen gelassen oder auf Zusatz eines Reduktionsmittels. Ein grüne Farbe wird erhalten bei pH unterhalb 10 und eine gelbe Farbe bei geringer Hypobromitkonzentration. Evidenz besteht dass Rh(VI) in der violetten und Rh(V) in der blauen Lösung anwesend sind. Die Disproportionierung 3 Rh(V) $\rightleftarrows$ 2 Rh(VI) + Rh(III) findet in saurem Medium statt.

Résumé—En présence d'hypobromite à pH 11, le rhodium donne une coloration violette, avec un maximum d'absorption à 530 mμ; cette coloration convient pour un dosage de 10–60 ppm de Rh, même en présence de platine. La solution vire au bleu per abandon ou par addition d'un agent réducteur, une couleur verte est obtenue à pH < 10 et une couleur jaune pour de faibles concentrations de BrO^-. L'auteur montre que Rh(VI) est présent dans les solutions violettes et Rh(V) dans les solutions bleues. La dismutation: 3 Rh(V) $\rightleftarrows$ 2 Rh(VI) + Rh(III) a lieu en milieu acide.

REFERENCES

[1] G. Grube *et al.*, *Z. Elektrochem.*, 1937, **43**, 397, 404.
[2] V. S. Syrokomsky and N. N. Proshenkova, *J. Anal. Chem. Russ.*, 1947, **2**, 247 (through *Analyst*, 1948, **73**, 361).
[3] G. H. Ayres and F. Young, *Analyt. Chem.*, 1952, **24**, 165.
[4] G. H. Ayres, *ibid.* 1953, **25**, 1622.
[5] D. Cozzi and F. Pantani, *J. Inorg. Nuclear Chem.*, 1958, **8**, 385 (chlorocomplexes).
[6] *Idem*, *J. Electroanalyt. Chem.*, 1961, **2**, 72 (bromocomplexes).
[7] *Idem*, *ibid.*, 1961, **2**, 230 (thiocyanate complexes).
[8] F. Pantani and P. Desideri, *Talanta*, 1960, **5**, 69 (thiourea complexes).

* In fact the *average* oxidation state should remain unchanged with the variation of pH.

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—IX*

THE DETERMINATION AND MASKING OF ALUMINIUM

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Summary—It has been found that aluminium forms complexes with 1,2-diaminocyclohexane tetra-acetic acid(CDTA)almost instantaneously, even at room temperature and in the presence of large excess of neutral salts. Contrary to general opinion, it is also possible to mask aluminium with ammonium fluoride at room temperature. If further determinations are being made with EDTA, a concentration of fluoride equivalent to the molar ratio 1:5 to 1:6 is sufficient for screening of aluminium. If the determinations are with CDTA it is necessary to add 30–50% excess of fluoride, corresponding to the molar ratio Al:F = 1:6. These findings has been utilised to develop a very simple and accurate method for the determination of aluminium and iron in their mixtures. Both determinations are based on the back-titration of an excess of EDTA with lead nitrate using Xylenol Orange as indicator. The further possibility of the determination of tervalent chromium, titanium and manganese in the presence of aluminium and iron has been discussed.

MANY papers have reported that the complexing of aluminium with EDTA is very slow, when carried out at ordinary temperature and in weakly acid medium. This is explained as resulting from the existence of strongly hydrated Al^{III} ions which, however, react quantitatively with EDTA at 100°. In the pH range 1–8 the predominant product of the reaction is the aquo-complex $[Al(H_2O)_2Y]^-$.

For this reason the complexometric determination of aluminium is mostly carried out indirectly; the solution of the aluminium salt is boiled with an excess of EDTA, and after cooling, the excess of EDTA is titrated with a metal salt using a suitable indicator. Direct titrations of aluminium so far described, using Chromazurol S[1] or PAN and the Cu-EDTA-complex[2] as indicators, are carried out almost at the boiling point. Various methods for determination of aluminium are described in a recent survey[3] and will not, therefore, be dealt with here.

Contrary to statements in the literature, however, we have found the reaction of aluminium with excess of EDTA to be virtually instantaneous even at ordinary temperatures, provided that no other neutral salts are present.[4] With increased ionic strength, however, the formation of the Al-EDTA complex is strongly retarded (see Table I). This finding is, of course, only of theoretical interest when determining aluminium in, for example, ores, which must first be decomposed by fusing with sodium hydroxide, potassium-sodium carbonates, sodium peroxide or similar materials. However, it is of much more interest that 1,2-diaminocyclohexanetetra-acetic acid (CDTA) reacts with aluminium quantitatively, even in the presence of high concentrations of sodium or potassium salts (see Table I). It is therefore possible to determine aluminium very simply, by adding CDTA to a weakly acid

* Part VIII: *Talanta*, 1961, **8**, 880.

solution of aluminium salt, adjusting the pH to 5–6 with hexamethylenetetramine, and back-titrating with lead nitrate using Xylenol Orange as indicator. The same conditions can be used for the determination of iron.

TABLE I.—DETERMINATION OF ALUMINIUM WITH EDTA AND CDTA
(Volume 150 ml.)

Neutral salt, *g*		Al taken, *mg*	Al found, *mg*	
			With EDTA	With DCTA
$NaNO_3$	0	6·55	6·57	6·55
	1		6·15	6·55
	3		6·04	6·57
	5		5·79	6·55
	10		5·07	6·53
	10[a]		6·02	6·52
	0	13·42	13·41 13·42	13·42 13·42
	1		13·37 13·38	13·42 13·39
	3		13·30 13·23	13·41 13·42
	5		13·17 12·93	13·36 13·49
	10		12·30 12·67	13·36 13·41
	10[b]		13·49 13·52	13·49 13·47
NaCl	1	6·55	6·53	6·54
	3		6·49	6·60
	5		6·49	6·55
	10		6·26	6·55
	10[a]		5·99	6·58

[a] Titrated after 1 hr [b] Titrated after boiling

Because of the simplicity of the procedure, it is of interest to investigate the conditions under which it would be possible to determine iron and aluminium in their mixtures. We therefore decided to re-examine the conditions necessary for the screening of aluminium with ammonium fluoride. For the masking of aluminium it is generally recommended that the solutions should be boiled with an excess of ammonium fluoride. This treatment gives rise to sparingly soluble cryolite. We have, however, found that aluminium can be reliably masked against EDTA, even in the cold, if the molar concentration ratio Al:F is as low as 1:5–1:6. When masking aluminium against CDTA, only a 30–50% excess is necessary, corresponding to the ratio Al:F = 1:6. The results of experiments with EDTA and CDTA given in Table II were obtained with "pure solutions" of aluminium salt, that is in the absence of excessive sodium or potassium salts.

Determination of Iron and Aluminium

Procedure

To the acid sample containing aluminium and iron add 0·05*M* CDTA in excess. Bring pH to 5–5·5 with hexamethylenetetramine, add several drops of 0·5% Xylenol Orange, and titrate with 0·05*M* lead nitrate. The consumption of CDTA gives the sum of Fe and Al.

To an aliquot of the solution add 1*M* ammonium fluoride (0·5–0·8 ml for 1 mg of Al). After 5 min add a measured volume of CDTA, adjust the pH again to 5–5·5 and titrate with 0·05*M* lead nitrate. The consumption of CDTA gives the content of Fe. Some results are given in Table III.

TABLE II.—MASKING OF ALUMINIUM WITH NH_4F AND DETERMINATION OF IRON

Taken, *mg*			Taken, *g*		Fe found, *mg*	Fe difference, *mg*
Al	Fe	F^-	$NaNO_3$	NaCl		
1·31	28·13	19	—	—	28·20	0·07
26·18	14·06	190	—	—	13·97	0·09
13·09	28·13	190	—	—	28·15	0·02
6·54	56·25	380	—	—	56·20	0·05
1·31	28·13	19	1	5	28·20	0·07
39·05	56·41	190	—	—	56·46	0·05
39·05	2·82	190	—	—	2·90	0·08
13·09	28·13	190	5	5	28·01	0·12[a]
6·54	56·25	380	5	1	56·31	0·06[a]
26·18	2·81	760	10	—	2·82	0·01[a]
39·05	56·41	190	2	5	56·60	0·19[a]
26·18	2·81	95	—	—	2·88	0·07[b]
26·18	2·81	9·5	10	—	6·01	3·20[c]

[a] Because of the high content of salts in the titrated solution (150–200 ml) it is advisable to speed up the screening of aluminium with fluoride by heating up to 50°. It is necessary only for the screening of aluminium, The salts do not interfere in the Al determination using CDTA.
[b] Ratio Al:F = 1:5.
[c] Insufficient fluoride was used.

TABLE III.—DETERMINATION OF ALUMINIUM AND IRON

Taken, *mg*		Found, *mg*		Difference, *mg*	
Al	Fe	Al	Fe	Al	Fe
7·07	18·10	7·12	18·27	0·05	0·17
1·41	18·10	1·43	18·15	0·02	0·05
28·25	9·05	28·40	9·18	0·15	0·13
14·12	1·81	14·15	1·92	0·03	0·11
14·12	18·10	14·13	18·08	0·01	0·02
7·07	54·26	6·99	54·29	0·08	0·03

Remarks: The colour changes in these titrations from yellow to red-violet or red (depending on the content of Fe), are very sharp. By means of this procedure even high concentrations of iron can be determined if the solution is sufficiently diluted. The limit of the amount of aluminium is 40 mg in 150–200 ml. Above this concentration the masking of aluminium by fluoride is not reliable, the colour changes are less sharp because of the blocking of indicator, and the results for iron are higher.

CONCLUSIONS

The determination of iron and aluminium with CDTA instead of with EDTA has the following advantages:

(*a*) The determination of the sum of aluminium and iron by indirect titration is carried out at normal temperature, this being so even in the presence of high concentration of sodium or potassium salts.

(*b*) The masking of aluminium by means of ammonium fluoride and the subsequent determination of iron is also carried out in the cold.

(*c*) Since the procedure is carried out at normal temperature, the two determinations are not affected by the presence of chromium[III].

(*d*) The determination of iron and aluminium is essentially simpler than the Sajó method,[4] which requires both a potentiometric apparatus and another indicating oxidation-reduction system.

Further experiments suggest that a simple procedure will be applicable in determination of titanium, chromium^{III} and manganese in one and the same solution. This will be described in the near future.

Zusammenfassung—Es wurde gefunden dass die Komplexbildung zwischen Aluminium und Diaminocyclohexantetraessigsäure (CDTE) auch bei Raumtemperatur und in Gegenwart grosser Mengen von Neutralsalzen praktisch momentan verläuft. Trotz allgemeiner Anschauung kann Aluminium mit Ammoniumfluorid auch bei Raumtemperatur maskiert werden. Bei einer Aluminiumbestimmung mit ÄDTE ist das Molverhältniss Al:F = 1:5 oder 1:6 zur Maskierung von Aluminium ausreichend. Bei der Bestimmung mit CDTE ist mindestens ein 30% iger Überschuss über das Verhaltnis 1:6 nötig. Diese Befunde wurden zur Ausarbeitung einer einfachen Methode für die Bestimmung von Eisen und Aluminium in Gemischen herangezogen. Beide Bestimmungen beruhen auf der Rücktitration von CDTE mit Bleinitrat unter Verwendung von Xylenolorange als Indicator. Die Möglichkeiten der Bestimmung von dreiwertigem Chrom, Titan und Mangan in Gegenwart von Eisen und Aluminium werden diskutiert.

Résumé—Les auteurs ont montré que l'aluminium forme pratiquement instantanément des complexes avec l'acide 1,2-diaminocyclohexane-tétracétique (CDTA) même à la température ordinaire et en présence d'un grand excès de sels neutres. Contrairement à l'opinion générale, il est possible de complexer l'aluminium par du fluorure d'ammonium à la température ordinaire. D'après un dosage ultérieur par l'EDTA, une concentration de fluorure égale au rapport molaire 1/5 à 1/6 est suffisante pour complexer l'aluminium. Pour le dosage par le CDTA, il est nécessaire d'ajouter 30–50% d'excès de fluorure qui correspond au rapport molaire Al/F = 1/6. Ces conclusions ont été utilisées pour mettre au point une méthode très simple et précise de dosage de l'aluminium et du fer dans leurs mélanges. Les deux dosages sont basés sur le titrage en retour de l'excès de CDTA par du nitrate de plomb, en utilisant le xylénol orange comme indicateur. Des possibilités nouvelles de dosages du chrome trivalent, du titane et du manganèse en présence d'aluminium et de fer ont été discutées.

REFERENCES

[1] M. Theis, *Z. analyt. Chem.*, 1955, **144**, 106.
[2] H. Flaschka and H. Abdine, *Ibid.*, 1956, **152**, 77.
[3] H. Flaschka, A. J. Barnard, Jr. and W. C. Broad, *Chemist-Analyst*, 1958, **47**, 22.
[4] M. Houda, J. Körbl, V. Bažant and R. Přibil, *Coll. Czech. Chem. Comm.*, 1959, **24**, 500.
[5] I. Sajó, *Acta Chim. Acad. Sci. Hung.*, 1955, **6**, 251.

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A pH-METRIC STUDY OF SOME BIVALENT METAL-5-SULPHOSALICYLIC ACID COMPLEXES

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Summary—The stabilities of 5-sulphosalicylate complexes of manganese, cobalt, nickel and copper have been studied at 25°, at constant ionic strength ($I = 0{\cdot}1$) using a cell without liquid junction. The values of log K obtained by the Bjerrum method are Mn: $pK_1 = 5{\cdot}25$, $pK_2 = 3{\cdot}4$; Co: $pK_1 = 6{\cdot}47$, $pK_2 = 4{\cdot}3$; Ni: $pK_1 = 6{\cdot}61$, $pK_2 = 4{\cdot}2$; and Cu: $pK_1 = 9{\cdot}35$, $pK_2 = 6{\cdot}92$.

SULPHOSALICYLIC acid is known to form stable soluble complexes with many metals. Turner and Anderson[1] reported the stability of the copper complex obtained by a spectrophotometric study. Perrin[2] obtained values for the relative stabilities of a number of metal complexes of substituted salicylic acids which are of physiological importance. Recently Banks and Singh[3] investigated the systems of 5-sulphosalicylic acid with copper, beryllium, cobalt and nickel. A titration technique was used by the last two groups of workers employing a glass electrode-calomel electrode system and no attempt was made to keep the ionic strength constant. It was thought desirable to study some of these complexes in a cell without liquid junction at a low constant ionic strength.

EXPERIMENTAL

Reagents

5-Sulphosalicylic acid (Hopkin and Williams) of m.p. 117°–119° was used. The solutions were standardised by pH titration with standard carbonate-free sodium hydroxide.

The metals were added in the form of their chlorides. Stock solutions of the AnalaR salts prepared in conductivity water were analysed for chloride gravimetrically as silver chloride. Duplicates agreed to $\pm 0{\cdot}02\%$. AnalaR potassium chloride was used to keep the ionic strength of all solutions constant at $0{\cdot}1M$.

Carbonate-free sodium hydroxide was prepared by dilution of saturated sodium hydroxide solutions (from pellets) in conductivity water freed from dissolved air by passing nitrogen and was preserved free from carbon dioxide with soda-lime guard tubes.

Grade A glassware was used in all the experiments.

Electrodes

The electrode system consisted of a wide-range glass electrode (Cambridge Instrument Co., "Yellow top") fitted with a B14 cone and a silver-silver chloride electrode. The latter was of the thermal-electrolytic type prepared by decomposing a paste of spectroscopically pure silver oxide (Johnson Mathey and Co.,) at 450° on a platinum helix fused into a glass tube fitted with a B14 cone. The platinum-glass seal was made by casting a little "Araldite" resin at the bottom of the electrode tubes. The silver was then chloridised in the absence of light by electrolysis in $1N$ hydrochloric acid solution prepared from constant-boiling acid, at a current density of 2 mA/cm^2 for approximately 2 hr. About 15 to 20% of chloridisation of the silver was thus ensured.[4] The electrode was then warmed in water at 50° for 2 hr.[5] and preserved in amber-coloured bottles in water containing a pinch of potassium chloride.

The electrode system was standardised in a buffer solution of $0{\cdot}1M$ ionic strength (and $0{\cdot}1M$ chloride concentration). A mixture of $0{\cdot}01M$ hydrochloric acid (prepared from constant-boiling acid) and $0{\cdot}09M$ potassium chloride has a pH of 2·10 at 25°.[6]

Cell (Fig. 1)

A B55 socket tube closed at one end has a bent jet inlet tube for bubbling pre-saturated oxygen-free nitrogen through the cell solution enabling the contents of the cell to be stirred well during the titration. The capacity of the cell is about 70 ml and an alternate inlet for nitrogen is provided for the cell above this level. A pre-saturator containing the cell solution and made integral to the cell is used for admitting nitrogen previously saturated with water vapour by passing through a gas-washing bottle. The nitrogen stream can be used to flush out the air in the cell and thus provide a carbon dioxide-free atmosphere. A B55 cone carrying three B14 sockets and a capillary exit tube forms the top of the cell. The glass electrode and the silver-silver chloride electrode are mounted on two of the B14 sockets. The alkali for titrations is in a semi-automatic grade A burette (capable of reading to 0·01 ml) fitted to a reservoir of standard sodium hydroxide. A B14 cone adaptor with a fine-drawn capillary tube enables the end of the burette to be fitted into the third B14 socket in the lid of the cell.

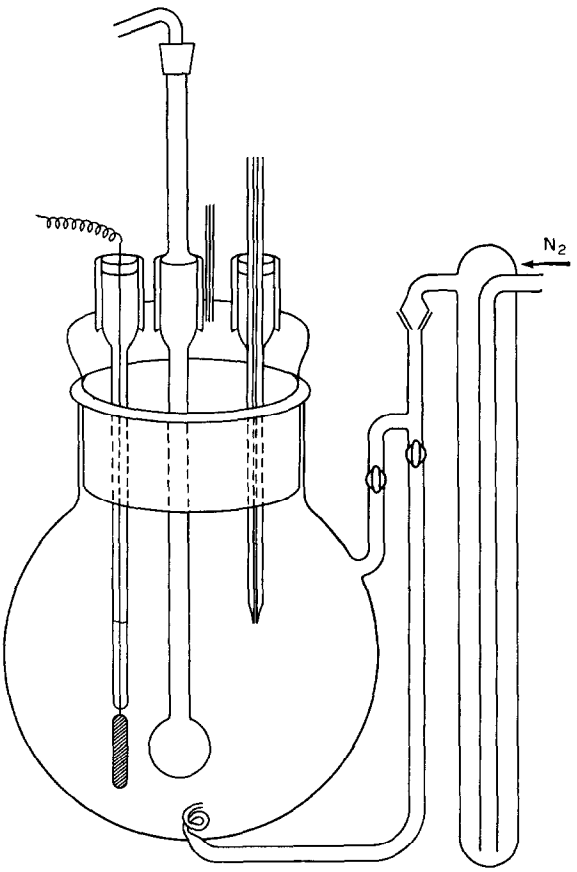


FIG. 1.—The cell

Solutions

Solutions were made up by volume in graduated flasks such that they were 0·1*M* in potassium chloride and 0·01*M* in sulphosalicylic acid and sodium hydroxide. These were the reference solutions, and the experimental solutions contained 0·002*M* bivalent metal chloride in addition to the above. Another set of experiments was carried out in 0·1*M* potassium chloride using 0·009*M* sulphosalicylic acid and sodium hydroxide, and 0·0015*M* metal chloride.

Procedure

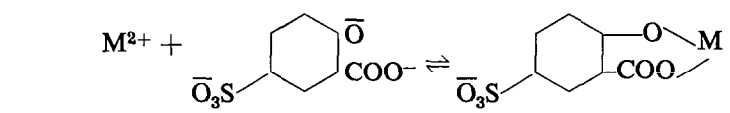
The cell used was:

Ag.AgCl|HCl|glass|Exptl. soln.(0·1*M* KCl, 0·01*M* H_3SSA, 0·01*M* NaOH. 0·002*M* MCl_2)|AgCl,Ag.

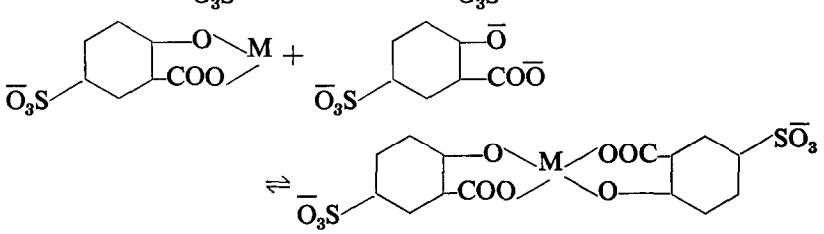
The electrode system was standardised with the HCl–KCl buffer solution (pH = 2·10 at 25°) in a thermostat. For the blank experiment 50 ml of the reference solution were taken in the cell, previously cleaned and dried, which was then introduced in a thermostat kept at 25 ± 0·05°. The calibrated electrodes were fitted on to the cell through the B14 sockets, and the alkali inlet was also introduced in a similar way so that the capillary nozzle was above the level of the liquid in the cell. Nitrogen ("white spot") saturated with water vapour was passed through the pre-saturator containing the solution at the same temperature as the cell, and allowed to bubble through the cell solution for about 15 min. The surface of the solution was flushed with nitrogen through the alternate inlet. The pH was measured. Small volumes of the standard alkali were added, the solution was stirred with nitrogen after each addition and the pH was measured after attainment of equilibrium. After the blank titration, the cell was washed and dried and the experiment was repeated using 50 ml of the experimental solution containing the bivalent metal. The standardisation of the electrode system was checked after every titration.

RESULTS AND DISCUSSION

The pH titration curves showed that separation between the reference and experimental curves occurred above pH 7·0, 6·2, 6·0 and 4·5 for manganese, cobalt, nickel and copper, respectively. Above pH 10, precipitation of the metal sulphosalicylate started in the cell. The pk_2 (carboxyl group) of 5-sulphosalicylic acid obtained from the pH at half-neutralisation being 2·86 at 0·1*M* ionic strength, the chelating agent may be regarded as completely dissociated to the $HSSA^{2-}$ form in the pH range 5 to 10. The additional amount of alkali required in presence of added metal salt to give the same pH as the reference solution, is used up in neutralising the hydrogen ion produced by the dissociation of the phenolic group as a result of chelation.



(1)



(2)

The overall reaction is therefore,

$$M^{2+} + 2\ SSA^{3-} = M(SSA)_2^{2-}$$

and the overall stability constant, β_2, is obtained as

$$\beta_2 = [M(SSA)_2^{2-}]/[M^{2+}]\ [SSA^{3-}]^2 = K_1 \cdot K_2,$$

where K_1 and K_2 are the equilibrium constants for the first and second stages. For evaluation of equilibrium constants of stepwise complex formation of this type, Bjerrum's method[7] could be employed very successfully. In this, a formation function $\bar{n}$ is defined as the average number of donor groups bound per metal ion present in any form. The function $\bar{n}$ was calculated from the additional amount of alkali required in presence of added metal to produce the same pH as in the blank titration (which is equivalent to the chelate formed) and the total concentration of metal ions at every stage of the titration. At any pH, the theoretical value of $[SSA^{3-}]$ was calculated from the value of k_3[9], the third dissociation constant of H_3SSA. Bjerrum has

shown that, as a first approximation, when $\bar{n} = 0{\cdot}5$, $1/[SSA^{3-}]$ equals K_1 and at $\bar{n} = 1{\cdot}5$, $1/[SSA^{3-}]$ equals K_2; in the simple case of two steps only, at $\bar{n} = 1{\cdot}0$, $1/[SSA^{3-}]^2 = \beta_2$. These relationships are strictly valid only when the spreading factor, x, between the successive formation constants, is more than 100, in which case the plot of $\bar{n}$ *vs.* $-\log_{10}[SSA^{3-}]$ shows the two steps completely separated. In the present work the formation curves were mostly of this form showing two distinct steps (*cf.* Fig. 2). The values for K_1, K_2, and β_2 obtained by this method are given in Table I.

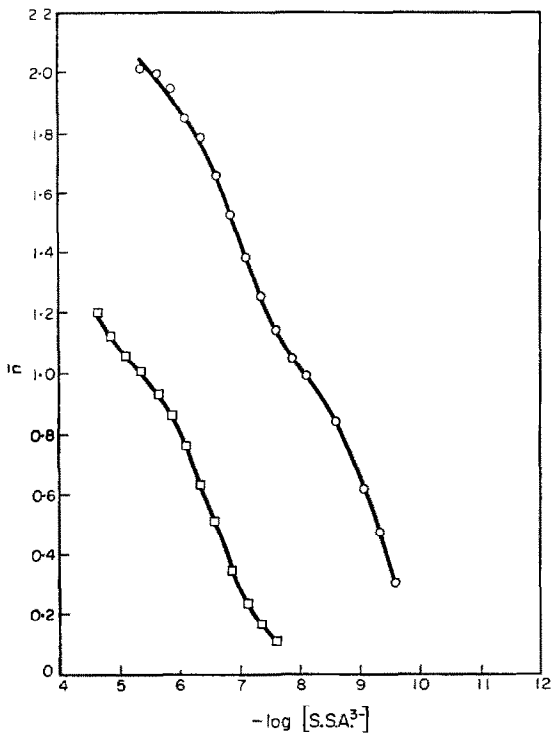


FIG. 2.—The formation curves for copper and nickel complexes, ○-Copper: □-Nickel.

TABLE I.—FORMATION CONSTANTS OF 5-SULPHOSALICYLATES OF TRANSITION METALS
(Ionic strength = 0·1)

Ion	$\log_{10} K_1$	$\log_{10} K_2$	$\log_{10} \beta_2$	2nd overall ionisation potential[8] E_2, *kcal*	Ionic radius,[8] *Å*
Mn^{2+}	5·25	~3·4	8·70	534·7	0·78
Co^{2+}	6·47	~4·3	10·76	586·0	0·74
Ni^{2+}	6·61	~4·2	10·80	599·0	0·73
Cu^{2+}	9·35	6·92	16·10	648·6	0·72

The K_2 values could not be determined directly except in the case of copper and may be slightly in error. No precipitation occurred in any of the experiments up to a pH of 10, but in the case of nickel the titration curve crossed that of cobalt at a pH of 8·5 and thereafter was between the manganese and cobalt titration curves. The K_2 values of cobalt and nickel are obtained very close to each other because of this. This is in apparent disagreement with the findings of Banks and Singh, who give the titration curves obtained with mixtures of $2{\cdot}5 \times 10^{-2}M$ H_3SSA and $2{\cdot}5 \times 10^{-3}M$ M^{2+}.

The $\log_{10}K_1$ and $\log_{10}\beta_2$ values increase in the order Mn, Co, Ni, Cu, in exactly the same way as have been found by Irving and Williams[8] for a number of neutral ligands, and for anions of weak acids complexing with the bivalent ions of the first transition series. Table I shows that this is the same order as is shown by the reciprocal of the cationic radius and by the second overall ionisation potential of the metals. These two parameters would be expected to determine the magnitudes of the electrostatic and covalent interactions, respectively. In those cases where the ligands interact with protons more strongly than does water, *i.e.* conjugate bases of weak acids, it may be assumed that the free energy of complex formation is dominated by the heat term in the relationship

$$\Delta G = \Delta H - T\Delta S$$

and that the entropy change would be of the same order for all the metal complexes in this series. It would, however, be desirable to determine the heat of complex formation, preferably by calorimetric methods, in order to obtain contribution to free energy from the entropy term, because of the partial charge neutralisation involved in complex formation between oppositely charged species.

Acknowledgement—The author wishes to thank Mrs. S. Taylor for laboratory assistance. The award of a Wilmot Breeden Fellowship is gratefully acknowledged.

Zusammenfassung—Die Stabilitätskonstanten der 5-Sulfosalizylsäurekomplexe von Mangan, Cobalt, Nickel und Kupfer wurden bestimmt bei 25°C und konstanter Ionenstärke von 0.1. Eine Zelle ohne Salzbrücke wurde verwendet. Die folgenden log K-Werte wurden nach der Bjerrummethode erhalten: Mn: $pK_1 = 5{\cdot}25$; $pK_2 = 3{\cdot}4$. Co: $pK_1 = 6{\cdot}47$; $pK_2 = 4{\cdot}3$. Ni: $pK_1 = 6{\cdot}61$; $pK_2 = 4{\cdot}2$. Cu: $pK_1 = 9{\cdot}35$; $pK_2 = 6{\cdot}92$.

Résumé—Les stabilités des complexes 5-sulfosalicylique du manganèse, du cobalt, du nickel et du cuivre ont été étudiées à 25°C, à force ionique constante (I = 0,1), en utilisant une cellule sans jonction liquide. Les valeurs de log K obtenues par la méthode de Bjerrum sont; Mn: $pK_1 = 5{,}25$, $pK_2 = 3{,}4$; Co: $pK_1 = 6{,}47$, $pK_2 = 4{,}3$; Ni: $pK_1 = 6{,}61$, $pK_2 = 4{,}2$; Cu: $pK_1 = 9{,}35$, $pK_2 = 6{,}92$.

REFERENCES

[1] S. E. Turner and R. C. Anderson, *J. Amer. Chem. Soc.*, 1949, **71**, 912.
[2] D. D. Perrin, *Nature*, 1958, **182**, 741.
[3] C. V. Banks and R. S. Singh, *J. Inorg. Nuclear Chem.*, 1960, **15**, 125.
[4] R. G. Bates, *Electrometric* pH *Determinations*. Wiley, New York, 1954, p. 204.
[5] J. H. Ashby, E. M. Crook and S. P. Datta, *Biochem. J.*, 1954, **56**, 190.
[6] H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*. Reinhold, New York, 1958, p. 712.
[7] J. Bjerrum, *Metal Ammine Formation in Aqueous Solution*. P. Haase and Son, Copenhagen, 1941.
[8] H. M. N. Irving and R. J. P. Williams, *J. Chem. Soc.*, 1953, 3192.
[9] V. S. K. Nair, *Trans. Faraday. Soc.*, in press.

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RADIOCHEMICAL SEPARATION OF INDIUM BY AMALGAM-EXCHANGE

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Summary—The radiochemical separation of indium by an amalgam-exchange technique has been critically evaluated for the aqueous hydrogen bromide system. The efficiency and contamination of the separation has been studied using tracers of 19 different representative elements. Yields of contaminating elements are reduced in most cases to less than 0·1%, and indium yields are usually above 95%. The procedure requires no special equipment, and takes about 11 min overall. A number of factors affecting the separation have been studied and improved.

THE principle of isotopic exchange between a metal ion and an amalgam of the metal has been applied to cadmium[1,3] and zinc[5] with considerable success. Preliminary work[1] also indicated that indium could be readily adapted to this type of separation. Sunderman and others[6,8] have given extensive yield and concentration data on a number of radiochemical separations of indium which can form a solid basis for a general evaluation of this amalgam-exchange method *versus* standard separation techniques.

A procedure has been developed for the aqueous hydrogen bromide system, which gives high yields of indium with good decontamination. Many factors which affect the procedure, such as concentrations of reagents, interferences, time of agitation, *etc.*, have been studied and evaluated.

The total separation procedure involves two isotopic exchange steps. In the first exchange, radioactive indium selectively exchanges with inactive indium in the mercury phase:

$$In(Hg) + In^{*3+} \rightleftarrows In^{*}(Hg) + In^{3+}.$$

The requirement here is that the concentration of indium in the amalgam should be much greater than the concentration of indium in the aqueous phase. The mercury phase is then removed, and the radioactive indium is back-exchanged into the aqueous phase by contact with higher concentrations of indium ion. Cobalt^{II} ion was also used for a few experiments in this back-exchange process.

EXPERIMENTAL

Apparatus

The separations are made in a 1/2-oz Boston-round bottle with polyethylene insert screw cap (available from Plax Corp., Bloomfield, Conn.). This is clamped in a mechanical shaker (Burrell Wrist-Action Shaker, Model 33) manufactured by the Burrell Corporation, Pittsburgh, Pa., to which an extension arm of 12 inches has been connected to give added radial action.

All radioactivity measurements were made with a Nuclear-Chicago Model DS-3 scintillation well counter as described previously.[2,6]

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Reagents

Amalgams: These were prepared by adding (under water purged with nitrogen) the appropriate weight of indium foil to 10 g of reagent-grade mercury which had been further purified by shaking with dilute nitric acid and rinsing 3 to 4 times with distilled water. The indium foil had also been subjected to dilute nitric acid and distilled water rinses before weighing.

Cobalt eluent solution: 100 mg of cobalt (as cobalt chloride) per ml in 0·4*N* hydrochloric acid.

Indium eluent solution: 10 mg of indium (as indium nitrate) per ml in 0·4*N* nitric acid.

Indium metal foil: 99·9% pure, Indium Corporation of America, Utica, New York.

Mercury: Baker and Adamson, triple distilled, analytical reagent.

Nitrogen gas: water-pumped, 99·99% pure, Liquid Carbonic Co.

All other non-radioactive reagents were of C.P. or analysed reagent grade.

All tracers used in this work have been described previously (Table II[7] and Table I[2]).

Amalgam-exchange procedure

Place 2 ml of 0·1*M* hydrobromic acid solution, containing tracers of contaminating ions (10^5 to 10^6 cpm) plus microgram amounts of inactive indium in a bottle. Chemical contamination added by the aliquots of contaminating tracers is negligible. Radioactive indium and non-radioactive interferences are used for yield determinations. Mix well. Add 0·5 ml of mercury as scavenger, cap the bottle, and shake for 1 min. Remove the mercury layer. Purge the system (both liquid and air above it in bottle) with nitrogen gas for 1 min. Add 75 μl (~1·0 g) of indium amalgam containing 0·2% of indium by weight (~2 mg). Quickly cap the bottle and shake mechanically for 4 min.

Decant the aqueous layer, transfer the amalgam to a new bottle, and wash twice with 2-ml portions of distilled water. Transfer the amalgam to a new bottle containing 2 ml of indium eluent solution. Add 0·5 ml of mercury to dilute the amalgam, cap the bottle, and shake mechanically for 5 min. Take a 100-μl aliquot of supernate for counting. The total time for separation is about 11 min.

Cobalt^{II} ion back-exchange procedure

Decontamination studies were also made employing cobalt^{II} ions as the eluent instead of indium. The procedure is the same as above except that a 2% (instead of 0·2%) indium amalgam was used and a 2-ml portion of the cobalt eluent solution was substituted in the final step for the indium eluent.

DISCUSSION AND RESULTS

A number of preliminary experiments were made to determine the optimum procedure to use for yield and contamination studies. Several solvent systems in addition to hydrobromic acid were investigated. For typical conditions 0·1*M* systems of HF, HCl, HBr, and HI gave yields of about 3%, 91%, 98%, and 97% respectively. The last two appear to give similarly high readings but the presence of free iodine in the HI system, as evidenced by discolouration, could lead to complications because of its oxidising character. Therefore hydrobromic acid was used.

Similar studies with different concentrations of HBr gave yields of 98%, 98%, and 79% for procedures using 0·5*M*, 0·1*M*, and 0·01*M* HBr respectively. Higher concentrations of acid generally tend to decrease the yield, and thus 0·1*M* HBr was used for the standard procedure.*

Failure to purge the system with nitrogen leads to a noticeable decrease in yield. For a 0·2% indium amalgam, however, only a fraction of a minute is required to rid the system of this oxygen effect. If no purging with nitrogen is performed, there is sufficient oxygen trapped in the bottle above the solution to oxidise indium from the amalgam into the aqueous phase on vigorous agitation, and thus to decrease the capacity of the amalgam for overall isotopic exchange.

* The results of these and other specific runs will be included in our AEC Progress Report No. 10, November, 1961, edited by R. S. Maddock and W. W. Meinke.

In the amalgam-exchange procedure, the separation of the radioisotope takes place by virtue of the rapid exchange which is known to occur between an element in the form of a dilute amalgam and its ions in solution. If there are many more inactive atoms of the element in the amalgam than there are of its radioisotope in solution, the amalgam exchange will result in most of the activity being incorporated into the amalgam.

Since the conditions used for these separations are far from ideal, experiments using different amounts of indium in the amalgam and in the aqueous layer indicate the limiting practical conditions which should be applied to this separation. Procedures using a 2% amalgam gave yields of 94–96% for concentrations of 0·4–50 μg of indium per ml in the aqueous solution. A slight reduction in yield to 90% was observed when this aqueous concentration was increased to 500 μg/ml.

With an aqueous concentration of ~2 μg of indium per ml, yields of about 97%, 96%, 90%, 44%, and 1% were obtained for amalgams containing 2%, 0·2%, 0·02%, 0·002%, and 0·0002% of indium, respectively. Since the results with 2% and 0·2% amalgams are about equally good, both have been used in some of the experiments.

Problems of air oxidation of the amalgam and of oxidation by microgram concentrations of the contaminants combine to reduce the yields at lower amalgam concentrations, so that it was felt that no smaller than 0·2% amalgam should be used for a general procedure.

Yields also depend upon the duration and type of agitation employed for the initial extraction and for the back-extraction. With the equipment mentioned above, yields increased regularly with time of shaking and levelled out after 3–4 min of agitation. In the back-extraction process there was a sharp rise until about 3 min with a gradual continuation of the rise after this time. Thus, the conditions chosen as optimum were a 4-min agitation for the initial extraction and a 5-min agitation for the back-extraction.

Methods other than shaking might be used to produce an intimate contact between the amalgam and the solution and thus to speed up this approach to equilibrium. Some preliminary studies have been made using an ultrasonic generator to disperse the drop of amalgam in the aqueous phase, but this method was so violent that it left some of the amalgam in suspension, and subsequent centrifuging was required to clear the solution.

The resultant optimum procedure has been outlined above. The degree of separation of indium obtained with this procedure from a number of elements representative of the periodic table is shown in Table I. For many of the elements the decontamination afforded was greater than could be measured with the levels of tracer used. It should be kept in mind, however, that these high decontamination values are in any case meant to give only a general indication of results, since at these levels, amounts of contaminants carried along are very dependent upon the techniques of manipulation.

These results are also plotted in Fig. 1 along with comparative values for decontamination by other methods such as bromide extraction, ion-exchange, and sulphide precipitation.[6] In general, the amalgam-exchange procedure gives somewhat better decontamination than the bromide extraction and considerably better than the other two methods. In addition, it is more convenient and less messy than the bromide extraction.

Some yield and decontamination values were also determined by the cobalt

TABLE I.—SEPARATION OF INDIUM AND CONTAMINANTS, AMALGAM EXCHANGE PROCEDURE[a]

Tracer[b]	Weight, μg[c]	Reduction potential, *volts*[d]	Separated, %
^{131}I	C.F.; I^-	[e]	<0·01
^{137}Cs	1	−2·92	<0·01
^{90}Sr-^{90}Y	C.F.	−2·89, −2·37	<0·01
^{144}Ce-^{144}Pr	C.F.	−2·48, −2·47	<0·01
^{95}Zr-^{95}Nb	C.F.	−1·53, −1·1	<0·01
^{182}Ta	970	−0·81	<0·01
^{65}Zn	200	−0·76	<0·01
^{51}Cr	2·5	−0·74	<0·01
^{115m}Cd	10	−0·40	0·7
^{204}Tl	420	−0·34	30
^{114m}In	3	−0·34	96·6 ± 0·5
^{60}Co	2	−0·28	<0·01
^{113}Sn	270	−0·14	28
^{124}Sb	3·5 (SbO^+)	+0·21	1
^{106}Ru-^{106}Rh	6 ($RuCl_5^{2-}$)	+0·60, +0·25	0·1
^{75}Se	11·5 (SeO_3^{2-})	+0·74	<0·01
^{192}Ir	1 ($IrCl_6^{2-}$)	+0·77	<0·01
^{203}Hg	140	+0·79	1
^{110}Ag	16	+0·80	0·04

[a] Average of duplicate runs except for indium, which is the average of five runs. Error is "standard deviation".
[b] Elements have been listed in order of their reduction potentials.
[c] Weight of inactive element present before separation. C.F. = carrier free.
[d] Standard reduction potential of lowest stable oxidation state to the elemental state. Data taken from Latimer.[4]
[e] Iodine is in its lowest reduced state.

eluent procedure. The indium and cobalt eluent systems appear to be comparable from the indium yield point of view but the indium eluent seems to give somewhat better decontamination for several of the elements.

The yield of the amalgam-exchange procedure can be affected by macro quantities of different reagents. The yield is quite insensitive to mineral acids, except for oxidising acids such as nitric acid in higher concentrations. Sulphates, phosphates, and alkaline materials decrease the yield considerably, as do oxidising agents in general. The fact that HBr is present in 0·1*M* amounts during the exchange procedure appears to "buffer out" some of the possible difficulties with certain reagents. For example, when HF is used alone at 0·1*M* concentration, a yield of only a few per cent is obtained whereas in the presence of 0·1*M* HBr the yield is above 90%. Some of these interference studies are summarised in Table II where the molarity of typical reagents is listed opposite the concentration near which the yield of indium appeared to drop below 85%.

Interferences from foreign cations appear to be small except where their reduction potential is such that they might be reduced by the amalgam or form precipitates with the reagents. When a cation is also an oxidising agent, additional problems are encountered and reduction to its lowest state by a reagent such as chromium^{II} sulphate is necessary before the exchange step should be attempted.[3]

The yield of selenium in Table I is surprisingly low in contrast to the 17% yields found in a study of the cadmium amalgam exchange procedure.[3] This discrepancy

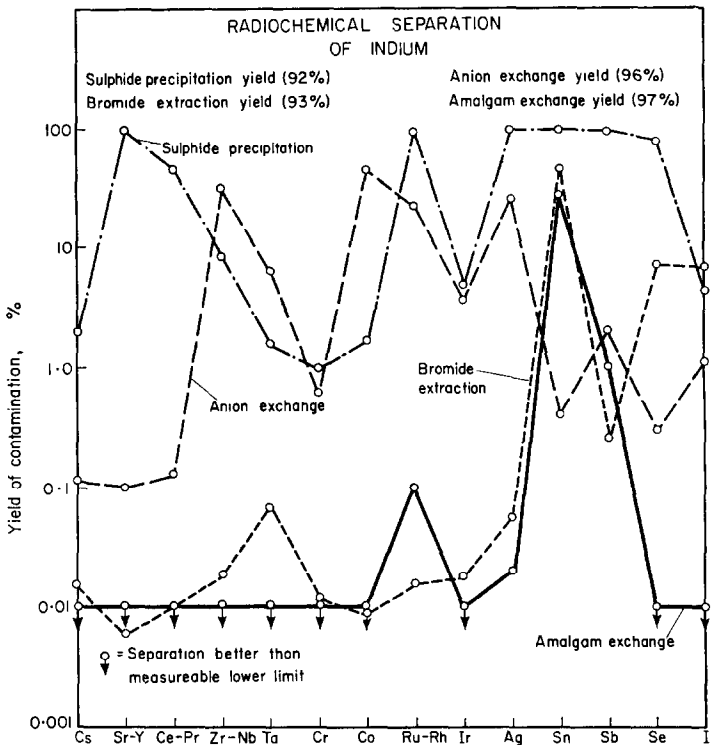


Fig. 1.—Experimental contamination for four types of indium separations.

is apparently caused by a difference in manipulation. In this indium work, the amalgam drop was brought into contact with an absorbent tissue to remove excess water after washing and before the back-extraction. At this point, the selenium, which upon reduction had formed a thin film on the surface of the mercury, mechanically rubs off on the tissue.

TABLE II.—INTERFERENCE SUMMARY, AMALGAM EXCHANGE PROCEDURE
(All taken in presence of 0.1*M* HBr)

Species	Molarity at which indium yield reduces below 85%
HF	2·5
HCl	10
HI	2
$HClO_4$	6
HNO_3	1·0
H_3PO_4	0·5
H_2SO_4	0·4
Na_2SO_4	0·25
NH_4NO_3	1·0
$NaClO_4$	0·25
Citric Acid	0·5
Sodium tartrate	0·05
Sodium acetate	1·0

The amalgam-exchange procedure for the separation of radioisotopes of indium is rapid and selective. It yields high decontamination from most elements and is relatively insensitive to interferences except for oxidising agents. It is somewhat better than the best previous radiochemical separation (bromide extraction) for this element and is more convenient to use since it avoids the necessity of working with inflammable ethers, and since the separation of phases is much more simple because of their high immiscibility.

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Zusammenfassung—Die radiochemische Abtrennung von Indium durch eine Methode mittels Amalgamaustausches wurde für das System Wasserstof-Bromid (in wasser) untersucht. Wirkungsgrad und Verunreinigungen der Trennung wurden studiert, wobei Tracer von 19 verschiedenen Elementen, verwendet wurden. Die Menge der Verunreinigung für die meisten Elemente wird auf 0·1 % reduziert während die Ausbeute an Indium für gewöhnlich über 90% bleibt. Die Methode benötigt keine besonderen Ausrüstungsgegenstände und der Zeitbedarf ist ungefähr 11 min. Eine Anzahl von Faktoren, welche die Trennung beeinflussen wurde studiert und die optimalen Bedingungen erarbeitet.

Résumé—La séparation radiochimique de l'indium par une technique d'échange sur amalgame a été examinée de façon critique pour le système aqueux hydrogène-bromure. L'efficacité et la contamination de la séparation ont été étudiées en utilisant des traceurs de 19 éléments représentatifs différents. Les rendements des éléments contaminants sont réduits dans la plupart des cas à moins de 0·1 %, cependant que les rendements d'indium sont d'habitude supérieurs à 95 %. La méthode ne nécessite pas d'équipement spécial et prend environ 11 minutes en tout. Un certain nombre de facteurs ayant une action sur la séparation ont été étudiés.

REFERENCES

[1] J. R. DeVoe, C. K. Kim and W. W. Meinke, *Talanta*, 1960, **3**, 298.
[2] J. R. DeVoe and W. W. Meinke, *Analyt. Chem.*, 1959, **31**, 1428.
[3] J. R. DeVoe, H. W. Nass, and W. W. Meinke, *ibid.*, 1961, **33**, 1713.
[4] W. Latimer, *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*. Prentice-Hall, Inc., New York, N.Y., 2nd edition, 1952.
[5] W. B. Silker, *Analyt. Chem.*, 1961, **33**, 233.
[6] D. N. Sunderman, I. B. Ackermann and W. W. Meinke, *ibid.*, 1959, **31**, 40.
[7] D. N. Sunderman and W. W. Meinke, *ibid.*, 1957, **29**, 1578.
[8] D. N. Sunderman and C. W. Townley, Nuclear Science Series Report NAS-NS-3014, *The Radiochemistry of Indium*, Office of Technical Services, Department of Commerce, Washington 25, D.C., May 1960.

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STERIC EFFECT OF *ortho*-SUBSTITUTED ALKYL GROUPS ON CHROMATOGRAPHIC ADSORPTION OF ANILINE*

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Summary—*Ortho* substitution of aniline can produce a variety of effects which dictate the behaviour of the molecule in chromatographic adsorption. The alkyl group thus substituted is clearly the best one through which to isolate the effect of blocking adsorption while minimising or eliminating other factors.

STERIC hindrance of an alkyl substituent has been shown to exert a marked influence on the chromatographic adsorption of *ortho*-alkyl substituted phenols.[1] LeRosen and co-workers[2] chromatographed a series of *ortho*- and *para*-disubstituted benzene compounds, but the influence of the second substituent was such as to enhance or impair the normal adsorption affinity of the first functional group in such a manner as to preclude quantitative evaluation of the factors involved. Among the factors to which this abnormal behaviour was attributed were steric hindrance, internal hydrogen bonding, and resonance and inductive effects.

The study of alkyl substituted anilines was undertaken to determine to what extent steric hindrance was effective in blocking adsorption of the amino group in aniline. The basicity of the amino group and its possession of two hydrogen atoms present a functional group capable of strong adsorption. As in the phenol study, the alkyl group was chosen as substituent because it would contribute nothing but steric hindrance as a factor in altering the normal adsorption of aniline.

EXPERIMENTAL

Reagents

N,N-Dimethylaniline, *N*-methylaniline, 2,6-dimethylaniline, *p*-toluidine, *o*-nitroaniline, *m*-nitroaniline, *p*-nitroaniline, *o*-phenylenediamine, *p*-phenylenediamine, *o*-chloroaniline, *m*-chloroaniline and *p*-chloroaniline were all Eastman White Label and were used without further purification. Aniline from open stock was purified by distillation from zinc dust at reduced pressure.

2,4,6-*Tri*-t-*butylaniline:* Prepared by the method of Bartlett, Roha and Stiles[3] from a sample of 1,3,5-tri-*t*-butylbenzene generously provided by Standard Oil of Indiana.

o-t-*Butylaniline and* p-t-*butylaniline:* The respective nitrobenzenes were prepared according to Craig[4] and reduced in the manner of Bartlett *et al.*[3]

o-*Isopropylaniline and* p-*isopropylaniline:* The respective nitrobenzenes were prepared by the method of Haworth and Barker[5] and reduced according to Bartlett *et al.*[3]

2,6-*Diethylaniline and* o-*ethylaniline:* Eastman Practical Grade reagent was dissolved in ether, precipitated with dry hydrogen chloride, and washed thoroughly with ether. The free amine was

* Much of the experimental work reported herein was performed while the authors were colleagues in the Department of Chemistry, Georgia Institute of Technology, Atlanta, Georgia, U.S.A.

liberated on dissolving in aqueous sodium hydroxide, then extracted into ether. After evaporation of ether the amine was distilled from zinc dust at reduced pressure.

o-Toluidine: Contaminating *p*-toluidine was removed by precipitation from ether solution with oxalic acid. After filtering, *o*-toluidine was precipitated with an excess of oxalic acid, washed thoroughly with ether, and finally liberated by the addition of aqueous sodium hydroxide. The free amine was isolated by ether extraction, the ether evaporated, and the amine distilled from zinc dust.

Solutions of the above anilines were prepared by weighing a small quantity of each amine into a glass-stoppered Erlenmeyer flask and adding sufficient benzene to make a 0·01*M* solution.

Adsorbents: Merck reagent grade silicic acid, and Florisil kindly donated by the Floridin Company, Tallahassee, Fla., were ground separately in a ball mill for 3 hr, then dried for 30 hr at 145°. Predetermined amounts of silicic acid and water were mixed intimately in a horizontal rotating cylinder to produce an adsorbent containing 12·75% water by weight. Florisil was treated similarly to bring its water content to 11·38% by weight.

Streak reagents: Cerium^{IV} nitrate was prepared in the manner of LeRosen *et al.*[6] *p*-Nitrobenzenediazonium tetrafluoroborate was prepared according to the directions of Cheronis and Entrikin.[7] Fresh 1% solutions in water were prepared daily.

Apparatus

Vacuum pump: Cenco Hyvac or any equivalent pump.

Chromatographic tubes: Number 1, precision bore, tapered tubes, 9 mm o.d. × 150 mm long, Scientific Glass Apparatus Co., Bloomfield, N.J.

Procedure

Adsorption columns were prepared by dry packing the chromatographic tube to a height of 75 ± 5 mm with adsorbent while applying full vacuum. Tapping the sides of the tube vigorously with a small wooden rod, and finally levelling the top of the adsorbent gently with the end of the rod, resulted in columns of sufficient reproducibility. A sample of 0·2 ml of the 0·01*M* aniline solution in benzene was applied to the top of the column and was followed immediately by a few drops of benzene. Two or three additional increments of benzene were introduced, precaution being taken not to allow the top of the column to become dry. Having worked the sample onto the column the void above it was filled with benzene and the developing process allowed to continue until solvent reached the bottom of the column. The vacuum was then shut off to the column, the upper assembly disconnected from the lower, and the adsorption column extruded from the chromatographic tube. Streaking the column with the appropriate colour producing reagent revealed the location of colourless anilines. At least duplicate runs were made on each of the anilines, the R values averaged, with the deviation of a single run being no greater than 0·02 from the average. Cerium^{IV} nitrate and *p*-nitrobenzenediazonium tetrafluoroborate were employed as streak reagents on each column.

DISCUSSION OF RESULTS

In studying the effects of various substituents upon the chromatographic adsorption of aniline it should be expected that geometric location of the substituent would play a significant role. It should be expected further that with the possible exception of the alkyl group several factors come into play, all contributing to an alteration of the normal adsorption of the amino group. Thus a nitro group or a chloro group will alter the basicity of the amino group through resonance or inductive effects, or both. This substituent effect on base strength is not reflected in an orderly manner in the chromatographic adsorption of the molecule, as examination of Table I shows. Confining the comparison to only *para*-substituted anilines or *ortho*-substituted anilines does not improve the correlation.

One might suspect that dipoles produced or intensified through substitution would, by altering the solubility characteristics of the adsorptive molecule in the developing solvent, give rise to orderly changes in R values as dipole moments or dielectric constants change. This does not prove to be the case.

TABLE 1.—R VALUES AND SOME pK_a VALUES OF SUBSTITUTED ANILINES ON SILICIC ACID ADSORBENT

Compound	R	pK_a
Aniline	0·25	4·58[a], 4·14[b]
o-Toluidine	0·30	4·39[a]
p-Toluidine	0·20	5·12[a]
o-Ethylaniline	0·34	
p-Ethylaniline	0·21	
o-Isopropylaniline	0·37	
p-Isopropylaniline	0·25	
o-*t*-Butylaniline	0·55	3·78[a], 3·39[b]
p-*t*-Butylaniline	0·25	4·00[b]
2,6-Dimethylaniline	0·35	3·42[c]
2,6-Diethylaniline	0·51	
2,4,6-Tri-*t*-butylaniline	1·00	2·00[b]
o-Nitroaniline	0·50	
m-Nitroaniline	0·27	
p-Nitroaniline	0·20	2·00[a]
o-Phenylenediamine	0·04	4·52[a]
p-Phenylenediamine	0·08	
o-Chloroaniline	0·72	2·13[c]
m-Chloroaniline	0·50	2·93[c]
p-Chloroaniline	0·42	3·46[c]
N-Methylaniline	0·50	4·40[a]
N,N-Dimethylaniline	0·56	4·26[c]

[a] In water at 25°.
[b] In 90% methanol.
[c] In 50% aqueous ethanol.

Ortho substitution in aniline would bring additional factors into consideration. Internal hydrogen bonding and steric hindrance are important among these. Again, however, interplay of such a variety of factors complicates the identification of any one as being paramount. Earlier works discuss at greater length some of the above-mentioned substituent effects.[2,8]

The steric effect can be isolated from the others by choosing the appropriate substituent. The alkyl group serves to accomplish this. Table I indicates that the R values of all of the *para*-alkyl substituted anilines are essentially the same. The absence of appreciable inductive or resonance effects with *para* substitution of the alkyl group validates the assumption that with the alkyl group substituted in the ortho position these effects are negligible. Yet, with the alkyl group substituted *ortho* to the amino group the R values increase significantly as the size of the alkyl group increases. Steric hindrance becomes particularly effective when alkyl groups are substituted on both *ortho* positions, as in dimethylaniline, 2,6-diethylaniline, and 2,4,6-tri-*t*-butylaniline.

The effect of *ortho alkyl* substitution on the chromatographic adsorption of phenols produced results which were qualitatively the same as those obtained in this study in which aniline provided the active adsorbing functional group. With the mechanism of adsorption of many functional group-bearing organic compounds generally accepted to lie in hydrogen bond formation between adsorptive and adsorbent,[2,8,9,10] the amino group with two hydrogen atoms would appear to possess a greater facility

than the phenol group to bond through active electron donor sites on the adsorbent. Compare the R values of the *ortho*-alkyl substituted anilines with those of the analogous phenols (Table II). The anilines are consistently more strongly adsorbed than the phenols.

TABLE 2.—R VALUES OF *ortho*-ALKYL SUBSTITUTED ANILINES AND ANALOGOUS PHENOLS

Substituent	R	
	Anilines	Phenols
o-Hydrogen	0·25	0·26
o-Methyl	0·30	0·37
o-Ethyl	0·34	0·43
o-Isopropyl	0·37	0·52
o-*t*-Butyl	0·55	0·74
2,6-Dimethyl	0·35	0·55

Regardless of the degree of coplanarity of the aniline molecule, some resonance energy has been gained at the expense of basicity by extending the resonance system of the ring to include the p_z electrons of the amino nitrogen. Thus a substituent which sterically hinders the coplanar arrangement of aniline would bring about a corresponding increase in the basicity of the molecule. Yet, basicity does not appear to be the over-riding factor. Consider the pK values and the R values of *o*-phenylenediamine, *p*-toluidine, and *N*-methylaniline in Table I. Although all are of approximately the same pK value, *o*-phenylenediamine exhibits a low R value consistent with the possession of a second active adsorbing group, *p*-toluidine exhibits an intermediate R value, and *N*-methylaniline exhibits a relatively high R value apparently as a result of substitution of an active hydrogen. Since the pK values and the R values of *N*-methylaniline and *N*,*N*-dimethylaniline are approximately the same it appears that both amino hydrogens are necessary for effective adsorption.

Zusammenfassung—Orthosubstitution von Anilin kann verschiedene Effekte verursachen, die für das Verhalten der Molekel bei chromatographischer Adsorption verantwortlich sind. Die Alkylgruppe ist klar die beste um den Effekt der Adsorptionblockierung zu isolieren, während andere Faktoren ausgeschlossen oder lediglich gemindert werden.

Résumé—On a examiné l'adsorption chromatographique de la molécule de l'aniline qui a été modifiée par l'ortho-substitution. Le groupe alkyl sert à distinguer entre les effets différents qui en resultent.

REFERENCES

[1] J. K. Carlton and W. C. Bradbury, *J. Amer. Chem. Soc.*, 1956, **78**, 1069.
[2] A. L. LeRosen, J. K. Carlton and P. B. Moseley, *Analyt. Chem.*, 1953, **25**, 666.
[3] P. D. Bartlett, M. Roha and R. M. Stiles, *J. Amer. Chem. Soc.*, 1953, **76**, 2349.
[4] D. Craig, *ibid.*, 1935, **57**, 195.
[5] R. D. Haworth and R. L. Baker, *J. Chem. Soc.*, 1939, 1299.
[6] A. L. LeRosen, R. T. Moravek and J. K. Carlton, *Analyt. Chem.*, 1952, **24**, 1335.
[7] N. P. Cheronis and J. B. Entrikin, *Semimicro Qualitative Organic Analysis*. Interscience Publishers, 2nd Ed., 1957, 730.
[8] W. A. Schroeder, *J. Amer. Chem. Soc.*, 1951, **73**, 1122.
[9] A. L. Elder and R. A. Springer, *J. Phys. Chem.*, 1940, **44**, 943.
[10] A. L. LeRosen, P. H. Monaghan, C. A. Rivet and E. D. Smith, *Analyt. Chem.*, 1951, **23**, 730.

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EMISSION SPECTRA FROM HIGH-FREQUENCY EXCITATION—II

THE SPECTRA OF NITROGEN, HYDROGEN AND AMMONIA

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Summary—The spectra of rarified samples of N_2, H_2 and NH_3, excited by a Tesla discharge, have been studied and found to be composed of known molecular band systems, strong atomic lines of hydrogen and impurity band systems. The significance of the results with a view to the analytical possibilities of the technique is discussed.

INTRODUCTION

IN the first publication in this series[1] the historical background to the use of a Tesla-type discharge for the excitation of spectra was discussed, and the development of a new apparatus and technique was outlined. This work has now been extended by an intensive study of the behaviour of a number of gases. In particular, this paper reports the results obtained using nitrogen, hydrogen and ammonia.

EXPERIMENTAL

Apparatus

High-frequency generator, vacuum train and sample cell: In this study the high-frequency generator, vacuum train and sample cell were similar to those previously described.[1] The Tesla-generator consisted of a radio-frequency transformer in a self-oscillating circuit at about 236 Kc/sec. with a Mullard QV06-20 valve. This generator produces an alternating voltage in the range 5–15 KV with low output power. The gases were energised by continuous excitation under low pressures.

The technique of sample introduction, pressure adjustment and control were also the same as described earlier.[1]

Measuring and recording instruments: Hilger Medium Quartz Spectrograph E498. Hilger Uvispek Photo-electric Spectrophotometer H700 with quartz prism. Hilger Non-recording Microphotometer L451 with Galvoscale ER300. Sunvic pen-recorder.

For qualitative or identification purposes, the plate from the spectrograph was run through the microphotometer attached directly to the recorder and a trace obtained which, when compared with a copper standard, enabled wavelengths to be assigned to peaks.

The microphotometer attached directly to the Galvoscale was used in the normal way for the quantitative estimation of the intensities of selected bands and lines.

The Uvispek spectrophotometer was used as a modified flame spectrophotometer with the flame source replaced by the glowing sample-tube. The responses were recorded on the Sunvic recorder.

Purification of gases: The gases were obtained from commercial cylinders, and had purity better than 99·9%. The gases were purified as far as possible, either by passing them through two liquid nitrogen traps or by condensing them in liquid nitrogen traps and re-distilling. This procedure was repeated twice.

Detection of spectra: In the procedure for the detection of the spectra, the sample-tube was attached to a vacuum train evacuated by a two-stage mercury diffusion pump backed by a rotary oil pump. The whole system was pumped out to a pressure of 10^{-4} mm of Hg, as measured on a Pirani gauge. The filling gas was allowed to sweep out the system, which was then pumped out again to 10^{-4} mm of Hg. The sample-tube was now isolated at 10^{-4} mm pressure, and the rest of the system was

filled with the gas under examination. On opening the sample-tube to the system, the gas flowed into it. The pressure in the sample-tube was now reduced, the high-frequency generator was switched on, and the pressure was altered until maximum glow was obtained.

Spectrophotometric investigations

The spectra of the glowing gases were examined with the spectrophotometer used as a modified flame spectrophotometer in which the normal flame source was replaced by the glowing gas. With the recorder attached, the responses were traced on the chart. Slit widths varied from 0·20 mm to 0·05 mm. The range of wavelength over which the glow was studied was 6100 Å to 2000 Å. The results obtained for the three gases are shown in Table I.

To interpret the above results obtained with the spectrophotometer, the spectra of the glowing gases were examined with the spectrograph.

Spectrographic studies

The spectrum of each gas was photographed with a slit width of 0·03 mm at an exposure time of 15 min. Ilford Ordinary N.30 and Panchromatic H.P.3 plates were used to examine the ultraviolet and blue regions, and the red regions of the spectra, respectively. The copper arc was employed as standard. The spectra were examined with microphotometer and recorder attachment, and with the Galvoscale. Wavelengths were assigned to the band heads obtained on the recorder chart by measuring the dispersion of the standard copper spectrum and using the relationship for the unknown band system. The trace of the standard copper spectrum is shown in Fig. 1 and that of nitrogen in Fig. 2.

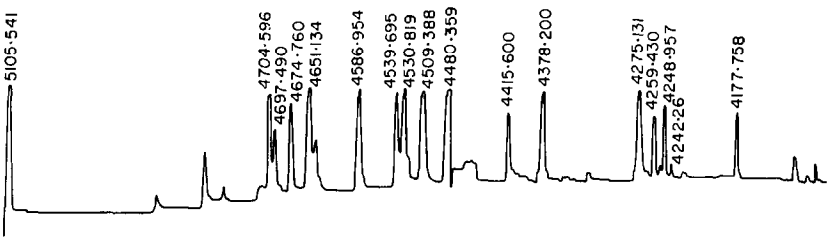


FIG. 1

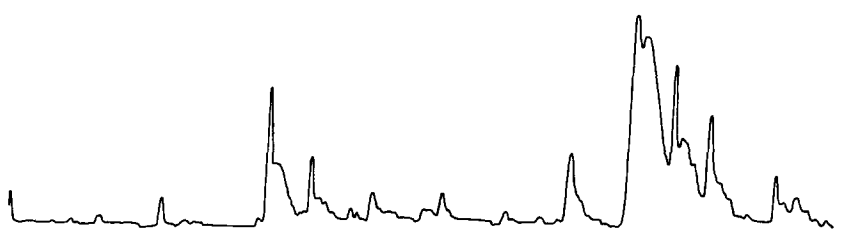


FIG. 2

RESULTS

In the method of measuring wavelengths by the procedure indicated above, there are experimental limitations so that an error of ± 5 Å can arise. This, however, did not prevent the assignment of the bands to known molecular band systems, and the atomic lines to elements. In this assignment Pearse and Gaydon's book[2] was used as the principal reference source.

The results from a series of experiments with the three gases were examined. The band systems and atomic lines which occurred are shown in Table II.

TABLE I

Gases	Band heads, Å (± 5Å)	Pressure, *mm of Hg*	Colour of glow	Nature of glow	Pressure for maximum intensity of glow, *mm of Hg*	Remarks
Ammonia	5430, 5380, 5260, *4860*, 4700 *4300*, 4280, 4060, *3910*, 3800, *3750*, *3580*, 3540, 3370, 3300, *3160*, 2980, 2820, 2420, 2300, 2190	0·5	Purple	Bright and stable	1·0–0·3	Glows down to a pressure of about 0·10 mm of Hg. The upper limit of pressure not determined. The most intense peaks are italicised.
Hydrogen	5610, 5200, *4860*, 4710, 4510, 4390, 4280, 4200, 4120, *3910*, 3710, 3640, *3370*, *3290*, 3130, 2980, 2880, 2820, 2300, 2190	0·4	Blue-violet	Bright and stable	1·5–0·3	Glows down to a pressure of about 0·15 mm of Hg. The upper limit of pressure not determined. The most intense peaks are italicised.
Nitrogen	5610, 5200, 4860, 4710, 4280, 4060, 4000, *3910*, 3800, *3760*, 3710, *3580*, 3540, *3370*, *3160*, 2980, 2880, 2300, 2190	0·4	Deep purple	Bright and stable	1·0–0·2	Glows down to a pressure of about 0·07 mm of Hg. The upper limit of pressure not determined. The most intense peaks are italicised.

TABLE II

Gas	Glow Pressure, *mm of Hg*	Observed molecular spectra and atomic lines
Ammonia	1·0–0·3	N_2 (second positive system); N_2^+ (main system); NH_2 (ammonia α bands); H_2 atomic line
Hydrogen	1·5–0·3	N_2 (second positive system); N_2^+ (main system); CN (violet system); CO (Angström system); CO^+ (first negative system); H_2 atomic line
Nitrogen	1·0–0·2	N_2 (second positive system); N_2^+ (main system); CN (violet system); CO (angstrom system); CO^+ (first negative system); H_2 atomic line

Interpretation of results

From the observations recorded in Table II, the results of Table I may be interpreted as follows:—

(1) *Ammonia.* The peaks at 5430 Å (5429·19 Å), 5380 Å (5384·64 Å) and 4700 Å (4702·18 Å; 4704·00 Å) are those of the NH_2 ammonia α-bands. That at 3370 Å is one of the NH bands. The strong peak at 4860 Å is that of the Hβ hydrogen line (4861·33 Å). All other peaks can be assigned to the other systems outlined in Table II.

The presence of the atomic line of hydrogen and the molecular bands of nitrogen would suggest the dissociation of ammonia into its components, nitrogen and hydrogen. They could possibly also arise from impurities. It is interesting to note that with time, the intensities of the NH_2 ammonia α-bands decreased, while those of nitrogen and hydrogen increased.

(2) The peaks in the hydrogen spectrum are from the strong atomic line of hydrogen 4860 Å (Hβ, 4861·33 Å) and those of the other systems indicated in Table II.

(3) The peaks of nitrogen are those of N_2 (second positive system), N_2^+ (main system), CN (violet system), CO (Angström system), CO^+ (first negative system).

DISCUSSION

From the results of this study, two significant points arise concerning the spectra produced by the Tesla-type discharge. The first is that the bands and lines which are excited can be ascribed to known systems. Thus, it can be shown that the results obtained by Given *et al.*,[1] arise in the main from well-known band spectra (*e.g.*, nitrogen) arising from impurities.

This leads to the second significant fact, which is that excitation of gaseous impurities is more readily achieved than excitation of the gas under study. In the present work, the occurrence of nitrogen band systems in the nitrogen and ammonia spectra are understandable, but their appearance in the hydrogen spectra can only be attributed to impurities. Experience has shown that heating an outgassed cell is sufficient to liberate impurities from the walls and give the characteristic nitrogen bands. In the first instance, the presence of the carbon monoxide and cyanogen bands was attributed to the black wax used to attach the quartz window to the sample cell, but later experiments with epoxy resin adhesive confirmed that these bands were

caused by desorbed impurities from the walls. Adsorption and desorption processes play significant roles in this technique. Baking of the cell and the high vacuum train at 400° under a pressure of 10^{-4} mm of Hg greatly reduces the impurities, but even then they interfere with the analytical possibilities of the method.

A number of the bands and lines in the spectra of the three gases were examined for linearity with pressure but, over the short range of pressure (from 1·5 mm to 0·2 mm) used, the intensity did not vary linearly with pressure. It increased to a maximum over a very short pressure range, and then decreased again. The position and magnitude of the maximum varied with the nature of the diluent gas. This confirms the findings of Steinberg and Poulson[3] that the sensitivity-pressure curves are parabolic in shape.

The present study also confirms the recent work of Heath,[4] who studied the relative intensities of the spectra from mildly excited discharges in N_2, air, NO, O_2, and mixtures of these gases at high resolution, as a function of pressure (0·01–760 mm of Hg). The gases were excited by means of an oscillator with a 1 kW, 200 Mc/sec output. Heath found that the parameter which largely determined the spectral characteristics was the gas pressure. He further found that the intensity of the second positive group of N_2 bands was reduced by more than a factor of 20 in an air discharge at atmospheric pressure, when compared to a corresponding discharge in pure N_2, and that the first positive group of N_2 bands was weakened in an air discharge at reasonably high pressure. The significance of these findings is that the intensity of emission is sometimes dependent on pressure and diluent gas, and some bands and lines are more sensitive to pressure than others. Again, some bands and lines are independent of pressure. In the development of this technique as a quantitative analytical method all these factors must be taken into consideration.

CONCLUSION

This study has shown that gases and vapours which are excited can be readily detected and identified by this technique. It holds promise, therefore, as a qualitative analytical tool with the advantage of sensitivity. However, while the characteristic molecular bands and atomic lines on photographic plates are one of the best means of identifying the species that produced them, their quantitative application, depending as they do on many variables, *e.g.*, nature of excitation, design of cell, photographic plate, time of exposure, *etc.*, is far from simple. To place the technique on a quantitative basis, therefore, requires (1) elimination of the impurities or their effect; (2) elimination of the effect of variation of pressure and temperature. This may mean working at constant pressure and temperature, or the selection of such bands or lines as are independent of pressure; (3) selection of bands free from interference by other systems present, or elimination of the effects of other systems present by careful control of experimental conditions; (4) use of instruments for measurement of the spectra which are capable of measuring intensities directly, ensuring greater speed, precision and accuracy than obtainable from the photographic methods of spectroscopy; and (5) elimination of the effect of diluent gases by careful calibration with standard mixtures of gases.

The requirements of (3) and (4) can be fulfilled by preliminary examination of spectra with the spectrograph, followed by examination with the spectrophotometer. Besides giving greater speed, the latter instrument gives better accuracy and precision,

since the spectrographic technique bases its accuracy and reproducibility on many variables, especially the behaviour of photographic emulsions.

At present, investigations are being carried out along these lines in this department. The results of this work will be communicated shortly.

Acknowledgement—One of us (C. L. C.) gratefully acknowledges the award of a research studentship from the Queen's University of Belfast which has made this work possible. Our thanks are also due to Dr. W. D. McGrath of this Department and Dr. W. F. Pickering of Newcastle University College, Technical University of New South Wales, at present working in this Department, for their advice on a number of matters, and for much helpful discussion.

Zusammenfassung—Die Spektren, angeregt durch eine Tesla-Entladung, von N_2, H_2 und NH_3 wurden studiert. Sie enthalten bekannte Molekülbanden, starke Atomlinien von Wasserstoff und Systeme von Verunreinigsbanden. Die Bedeutung der Befunde im Hinblick auf analytische Verwertung wird diskutiert.

Résumé—Les auteurs ont étudié les spectres d'échantillons raréfiés de N_2, H_2 et NH_3 excités par une décharge Tesla; ces spectres sont composés de systèmes de bandes moléculaires connues, de raies atomique intenses d'hydrogène et de systèmes de bandes d'impureté. La signafication des résultats est discutée; les auteurs donnent une idée des possibilités analytiques de la méthode.

REFERENCES

[1] Thomas Given, Robert J. Magee and Cecil L. Wilson, *Talanta*, 1959, **3**, 191.
[2] R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra*. Chapman and Hall Ltd., 2nd Edition Revised, 1950.
[3] J. C. Sternberg and R. E. Poulson, *J. Chromatog.*, 1960, **3**, 406.
[4] D. R. Heath. U.S. Atomic Energy Commission, LA.2335, 1960.

Talanta, 1962, Vol. 9, pp. 49 to 51. Pergamon Press Ltd. Printed in Northern Ireland

PRECIPITATION OF METAL 8-HYDROXYQUINOLATES FROM HOMOGENEOUS SOLUTION—V
MAGNESIUM

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Summary—A method has been developed for the precipitation of magnesium 8-hydroxyquinolate from homogeneous solution with 8-acetoxyquinoline. Satisfactory separations from sodium, potassium, and barium were obtained.

INTRODUCTION

MAGNESIUM 8-hydroxyquinolate was first precipitated in 1910 by Fox,[1] who added an aqueous solution of 8-hydroxyquinoline and sodium hydroxide to a neutral solution of magnesium acetate. Many investigators have subsequently recommended gravimetric methods in which 8-hydroxyquinoline is used to determine magnesium. The formula of the precipitate dried at 110 ± 10° is said to be $Mg(C_9H_6ON)_2 \cdot 2H_2O$. The anhydrous form is reported to exist above 130°; the usual recommended temperature for weighing the precipitate in this form is 150 ± 10°.[2,3]

The purpose of this investigation was to develop a method of precipitation from homogeneous solution for magnesium using 8-acetoxyquinoline and to determine the effect of some diverse ions.

EXPERIMENTAL

At temperatures above 5–10°, 8-acetoxyquinoline hydrolyzes too rapidly so that precipitation occurs almost instantly. When the pH is below 10·0, precipitation is incomplete (*cf.* Table I). The crystals formed at low pH values are darker in colour and coarser in texture.

Satisfactory results for analytical purpose were obtained by the dropwise addition of 2·1 ml of a solution containing 0·42 g of 8-acetoxyquinoline (20% excess over the stoichiometric quantity required for 25 mg of magnesium) to a cold, ammoniacal solution containing magnesium and allowing the reaction mixture to stand for 2·25 hr followed by a short warming period. Three to four min were required for the dropwise addition (burette with Teflon stopcock) of 8-acetoxyquinoline; initial precipitation of the magnesium would usually begin when the last of the reagent had been added. Other derivatives of 8-hydroxyquinoline were not tested for rate of hydrolysis; however, some related exploratory work was attempted with derivatives of 8-hydroxyquinaldine. Only one of the latter, 8-benzoxyquinaldine, was prepared in crystalline form but it was found to hydrolyse too slowly for precipitation purposes.

Reagents

Magnesium: Reagent grade $MgCl_2 \cdot 2H_2O$. (J. T. Baker Chemical Company, Phillipsburg, New Jersey). The concentration of the standard solution was determined by precipitation of the magnesium as the oxalate and titration with potassium permanganate.[4]

Calcium: Reagent grade $CaCl_2$. (J. T. Baker Chemical Company, Phillipsburg, New Jersey).

Barium: Reagent grade $BaCl_2 \cdot 2H_2O$. (J. T. Baker Chemical Company, Phillipsburg, New Jersey).

Sodium: Reagent grade NaCl. (Mallinckrodt Chemical Works, St. Louis, Missouri).

Potassium: Reagent grade KCl. (J. T. Baker Chemical Company, Phillipsburg, New Jersey).

8-Hydroxyquinoline: (Matheson, Coleman, and Bell Division of Matheson Company, East Rutherford, New Jersey). An acetic acid solution of the reagent was used to precipitate magnesium in the conventional manner as described by Kolthoff and Sandell.[5]

8-Acetoxyquinoline: PFHS grade (Burdick and Jackson Laboratories, 1953 Harvey St., Muskegon, Michigan).

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TABLE I.—PRECIPITATION OF MAGNESIUM 8-HYDROXYQUINOLATE

Number	1	2	3	4	5	6	7	8	9	10	11	12	13
Method of precipitation	conventional	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS	PFHS
Modifications in precipitation procedure	a,h	b,h	c,h	i	h,i	h,i	h,i	h,i	h,i	h,i	h,i	h,i	h,i
Diverse element taken, *mg*	none	none	none	none	none	none	none	none	Na 1000	K 1000	Ba 200	Ba 50	Ba 15
Magnesium taken, *mg*	11·94	11·94	9·77	12·32	2·57	5·14	12·32	25·68	12·84	12·84	12·84	12·84	12·84
Difference, *mg*	−0·14 −0·07 −0·14	−0·11 −0·12 −0·14 +0·07 +0·14	−0·09 −0·09 −0·08	−1·58[a] −0·16[e] −0·54[f] −0·10[g]	+0·01 −0·03 0·00 −0·05	+0·01 −0·05	−0·04 −0·03 −0·06	−0·11 −0·15	+0·16 +0·13 +0·03	−0·05 −0·07	+1·48 +1·36 +1·96	+0·21 +0·42	−0·05 +0·06

[a] 4x stoichiometric quantity of 8-hydroxyquinoline added.
[b] 3x stoichiometric quantity of 8-acetoxyquinoline added.
[c] 2x stoichiometric quantity of 8-acetoxyquinoline added.
[d] pH 8.5
[e] pH 9.0
[f] pH 9.5
[g] pH 10.5
[h] pH 10.0
[i] 0.42 g of 8-acetoxyquinoline added = 1.2x stoichiometric quantity required for 25 mg of magnesium.

Procedure

Dilute a nearly neutral solution containing 5 to 25 mg of magnesium to approximately 125 ml with distilled water. Add 4 ml of 3*N* hydrochloric acid and adjust to pH 10·0 with filtered 1:1 ammonium hydroxide. Adjust the final volume to 150 ml. Cover the beaker with a watch glass and allow to stand in an ice bath for 15 min. Slowly add, with stirring, 2·1 ml of an acetone solution containing 1·0 gm of 8-acetoxyquinoline per 5·0 ml of acetone. Allow to stand at room temperature for 2·25 hr with occasional stirring. Heat the solution to 50–60° for 20 min before filtering through a medium-porosity filtering crucible. Wash the precipitate with a 1% ammonium hydroxide solution. Dry at 105° ± 1° for 2 hr and weigh as $Mg(C_9H_6ON)_2 \cdot 2H_2O$ or at 155° ± 1° for 2 hr and weigh as $Mg(C_9H_6ON)_2$; the gravimetric factors are 0·0698 and 0·0778, respectively.

RESULTS AND DISCUSSIONS

The results shown in Table I were obtained using the procedure given, concluding the determination by drying the precipitate at 105°. Although good results were obtained with less than 5 mg of magnesium present, *i.e.* with 2·57 mg, excess 8-hydroxyquinoline also tended to precipitate. The recommended procedure proved satisfactory for 5 to 25 mg of magnesium.

The drying temperature of 105 ± 1° for the dihydrate is somewhat critical. Precipitates dried at 110° gave low values for magnesium. Both a chemical analysis by bromination of the precipitate and thermal studies indicated that $Mg(C_9H_6ON)_2 \cdot 2H_2O$ loses some water at 110°. Further work showed that the precipitate could be weighed as the anhydrous material after drying at 155° for 2·5 hours.

Spectrophotometric determination of magnesium[6] in the filtrate and wash solution showed that the combined solubility loss is approximately 0·02 mg when 12·32 mg of magnesium were precipitated according to the procedure.

Table I shows that 12 mg of magnesium can easily be separated from 1000 mg of sodium or potassium and 15 mg of barium; a separation from 200 mg of calcium was not successful.

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Zusammenfassung—Eine Methode wurde entwickelt um Mg-oxinate aus homogener Lösung zu fällen, wobei 8-Acetoxychinolin verwendet wird. Zufriedenstellende Trennung von Na, K und Ba ist erzielbar.

Résumé—Les auteurs ont mis au point une méthode de précipitation du 8-hydroxyquinoléate de magnesium en solution homogène par la 8-acétoxyquinoléine. Des séparations satisfaisantes du sodium, du potassium et du baryum ont été obtenues.

REFERENCES

[1] J. J. Fox, *J. Chem. Soc.*, 1910, **97**, 1119.
[2] C. Duval, *Inorganic Thermogravimetric Analysis*. Elsevier Publishing Co., New York, 1953, p. 102–3.
[3] R. G. W. Hollingshead, *Oxine and its Derivatives*. Butterworths Scientific Publications, London, 1954, vol. 2, p. 323.
[4] L. Gordon and E. R. Caley, *Analyt. Chem.*, 1948, **20**, 560.
[5] I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*. The Macmillan Company, New York, 3rd ed., 1952, p. 363.
[6] E. B. Sandell, *Colorimetric Determination of Traces of Metals*, Vol. III. Interscience Publishers, Inc., New York, 3rd ed., 1959, pp. 599–600.

Talanta, 1962, Vol. 9, pp. 53 to 63. Pergamon Press Ltd. Printed in Northern Ireland

THE COMPLEXOMETRIC DETERMINATION OF PLUTONIUM IN REACTOR FUEL PROCESSING PLANT SOLUTIONS—I*

NITRIC ACID SOLUTIONS OF IRRADIATED URANIUM

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Summary—An accurate and precise method for the determination of plutonium in nitric acid solutions of irradiated uranium is described. Plutonium^{IV} is extracted using the quaternary amine Hyamine 1622 dissolved in benzene; the benzene is removed by evaporation and, after dissolution of the residue in acetone, an excess of ethylenediaminetetra-acetic acid (EDTA) is added and the uncomplexed EDTA determined by photometric titration using standard zinc chloride solution and dithizone as indicator. The extraction is highly specific for plutonium and a two-stage cycle results in a decontamination factor of approximately 10^5 for mixed fission products and 10^2 for uranium. Under carefully controlled conditions the method yields a standard deviation of 0·4% for 10^3-μg amounts of plutonium.

INTRODUCTION

THE safe and efficient operation of a chemical process for the separation and purification of plutonium from irradiated uranium requires extensive analytical control. Of particular importance is the precise and accurate determination of plutonium at selected stages of the process. Inherently the most difficult problem is the determination of plutonium in nitric acid solutions of the fuel elements which constitutes the feed solution to the processing plant. Such solutions, which are considered in this paper, contain uranium in several thousand-fold excess of the plutonium, and fission product $\beta\gamma$-activity of approximately 15 mc per ml of solution. A second paper will deal with solutions arising after several stages of the separation process and which contain approximately equal amounts of plutonium, uranium, iron and chromium at much reduced levels of fission product radioactivity.

Methods for determining plutonium in impure solutions of this type fall into two main groups, radiometric and chemical. Radiometric methods usually involve the counting of α-particles from a suitably diluted portion of the sample.[1] This approach is virtually independent of the non-radioactive constituents of the sample unless these are present in sufficient concentration to lead to serious absorption of α-particles in the source prepared for counting. The technique has the disadvantage of requiring correction for the α-particle contributions from transplutonium elements (in particular americium-241 and curium-242) and also uranium if present in sufficient quantity, and these corrections must be separately determined. Further, the conversion of counting rate to mass of plutonium requires an ancillary determination of an accurate specific activity of the plutonium. Clearly this conversion can prove troublesome when processing fuel of widely varying irradiation history.

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Chemical methods such as absorptiometry,[2,3] coulometry[4,5,6] and redox titrimetry,[7] circumvent these difficulties but they require a much larger sample and in consequence necessitate fully or semi-remote handling, at least in the early stages of the procedures. In addition, when applied to impure solutions of the type under discussion they invariably require a complete preliminary separation of the plutonium. However, in view of their inherently greater accuracy considerable attention has been devoted to chemical methods in recent years. The isotope dilution method recently described by Webster *et al.*[8] offers an interesting alternative in which complete chemical isolation of the plutonium is not required.

In the Windscale laboratories the plutonium content of solutions of irradiated uranium has been determined absorptiometrically using the coloured complex formed by plutonium^{IV} with thoronol [1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulphonic acid][9] and 50–100 μg of plutonium for each determination. The preliminary separation is achieved by extracting the plutonium from a 2–4*M* nitric acid into a solution of Hyamine 1622 in benzene. Hyamine 1622 is essentially *p*-di-isobutylphenoxyethoxy-ethylbenzyldimethylammonium chloride and its behaviour as an extractant has been studied in detail by Powell.[10] It extracts plutonium as the anionic species $Pu(NO_3)_6^{2-}$ and provides an extremely selective means of separating plutonium since few elements form anionic nitrates in 2–4*M* nitric acid. The complete method yields a standard deviation of 1·4% at the 100-μg plutonium level and thus compares favourably with other non-differential absorptiometric methods for other elements.

It was considered that improved precision would result by replacing the absorptiometric finish by a titrimetric one, whilst retaining the initial Hyamine 1622 separation. Ethylenediaminetetra-acetic acid (EDTA) was selected for study since it forms strong 1:1 complexes with all valency states of plutonium[11,12] thereby obviating a valency conditioning step. In addition it forms only weak complexes with the uranyl ion[13] and consequently the small amounts of uranium co-extracted with the plutonium should not interfere. Milner and Woodhead[14] have shown that milligram amounts of plutonium as plutonium^{III} can be successfully determined using EDTA. The present procedure has been developed to give precise and accurate results using 100–200 μg of plutonium contained in a solvent phase. It involves adding EDTA in excess of the plutonium to an acetone solution of the Hyamine 1622 extract and back-titrating with standard zinc solution to a dithizone end-point.

EXPERIMENTAL

Apparatus

Extraction apparatus: The extraction unit is shown in Fig. 1. It comprises two vessels attached to a manifold which enables them to be filled and emptied through a capillary swan-necked side-arm by applying suction or compressed air. Mixing of solutions in the vessels is promoted by drawing air through the capillary into the body of the vessel. The cone and socket joints are kept free of grease to avoid introducing titratable impurities into the system.

Photometric titration apparatus: This is shown diagrammatically in Fig. 2 and the titration cell is shown in detail in Fig. 3. The conical cell, fitted with a few coils of resistance wire to provide gentle heating for the evaporation stage, is situated between an ordinary filament lamp and a photoelectric cell connected to Cambridge galvanometer through a variable resistance. An Ilford 604 filter having maximum transmission at 510 mμ was placed between the titration cell and the photocell since the pink end-point colour of the zinc—EDTA titration shows maximum absorbance at this wavelength. The contents of the cell are stirred by means of compressed air bubbled through a glass dip tube drawn out to a fine jet.

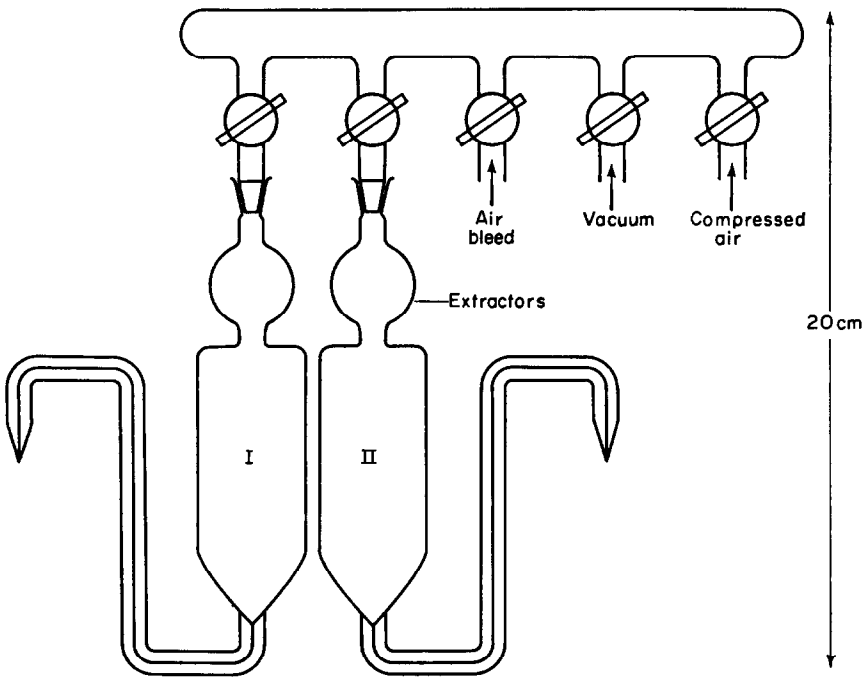


FIG. 1. Extraction apparatus.

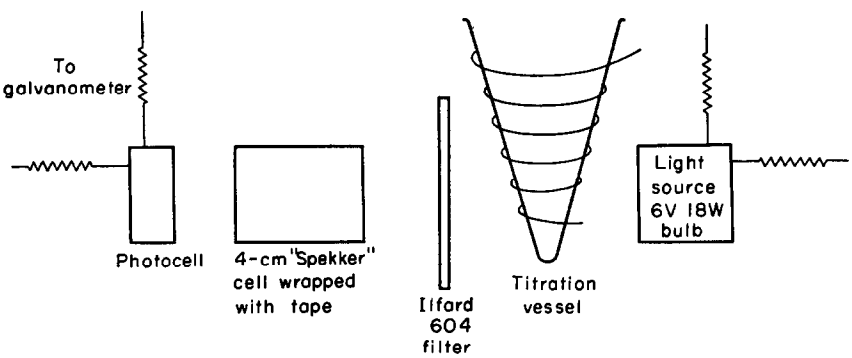


FIG. 2. Photometric titration assembly.

Remotely controlled pipette: For the remote handling of radioactive solutions a capillary pipette of the type shown in Fig. 4 was used. Application of suction draws the solution into the pipette until it just overflows the fine-capillary top. When the overflow ceases the measured volume is ejected. Two pipette washings were carried out for each sampling by drawing up and ejecting wash liquor in the same manner but not allowing it to overflow at the top.

Microburettes: Agla microburettes of 0·5-ml capacity were used. The one used to deliver standard zinc chloride solution was calibrated over the full range of drum readings. The second burette, used to deliver a fixed volume of EDTA solution was not calibrated, but always used over the same scale range.

Reagents

1% *w/v Hyamine* 1622 *solution in benzene:* 0·5 g of Hyamine 1622 (supplied by Rohm and Haas Co. Ltd.) was dissolved in 5 ml of water and the nitrate precipitated by adding 5 ml of 3*M* nitric acid.

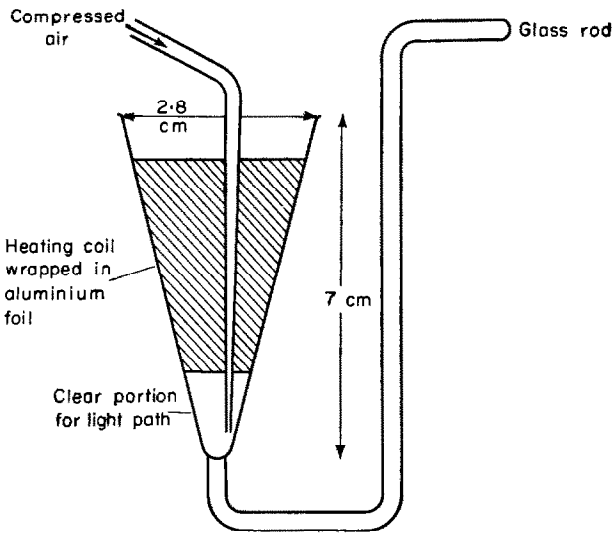


FIG. 3.—Titration cell.

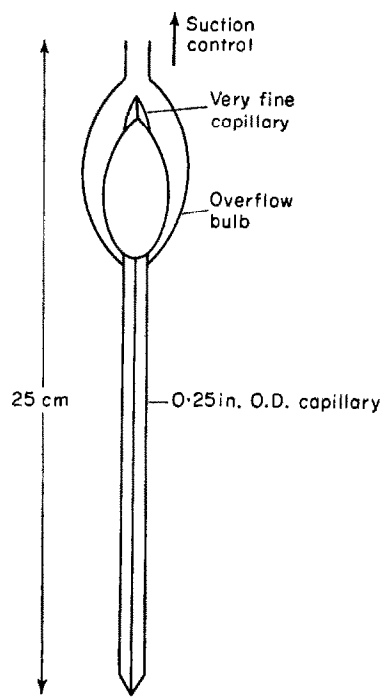


Fig. 4.—Remotely operated pipette, 2-ml capacity.

After decanting off the supernate the white curdy precipitate was dissolved in 50 ml of twice distilled benzene. The suspended aqueous phase was removed by filtration through a Whatman No. 41 filter paper moistened with benzene.

All other reagents were of AnalaR quality where possible. The standard 0·004*M* zinc chloride solution, the 0·04% w/v dithizone solution in acetone and the 10% iron^{II} ammonium sulphate solution (0·004*M* in sulphuric acid) were prepared freshly each day.

Extraction of plutonium by Hyamine 1622 *in benzene*

Plutonium^{IV} is the only valency state of plutonium efficiently extracted by this solvent, the approximate partition coefficients being greater than 200, 0·2 and very low for plutonium^{IV}, ^{VI} and ^{III} respectively. Consequently the success of the procedure depends on complete conditioning to plutonium^{IV} before extraction. The samples to be analysed comprised primarily plutonium^{IV} with some plutonium^{VI}. Iron^{II} ion was chosen as the reductant since it operates efficiently at room temperature. Hydrogen peroxide, demonstrated to be an efficient conditioning agent by Ockenden and Foreman,[15] was rejected for the present work since it involves prolonged heating in 7–8*M* nitric acid.

Optimum conditions for complete conversion to plutonium^{IV} were established using a synthetic solution containing approximately 10% of plutonium^{VI}, 90% of plutonium^{IV} (total concentration 88·2 μg/ml) in 3*M* nitric acid. The results quoted in Table I were derived by extracting a 2-ml portion of this solution twice with 2-ml volumes of 1% Hyamine 1622 in benzene for 1·5 min under the stated

TABLE I.—CONDITIONING TO PLUTONIUM^{IV} USING IRON^{II}

All experiments performed on a solution containing 160 μg of plutonium^{IV} and 18·5 μg of plutonium^{VI} in 2 ml of 3*M* nitric acid

Experiment no.	Conditions	Plutonium in aqueous phase, μg	
		After one extraction	After two extractions
1	No Fe^{2+} present	13·5	10·5
2	No Fe^{2+} present	15·0	10·0
3	0·3 ml of 10% iron^{II} ammonium sulphate added before first extraction	6·9	0·2
4	0·3 ml of 10% iron^{II} ammonium sulphate added before first extraction	7.3	0·16
5	0·3 ml of 10% iron^{II} ammonium sulphate added after first extraction	14·0	2·4
6	0·3 ml of 10% iron^{II} ammonium sulphate added after first extraction	13·6	2·0
7	0·3 ml of 10% iron^{II} ammonium sulphate added after first extraction	14·0	(10·0)*
8	0·1 ml of 10% iron^{II} ammonium sulphate added before first extraction	14·0	3·0
9	0·5 ml of 10% iron^{II} ammonium sulphate added before first extraction	14·8	0·3

* High results caused by use of aged iron^{II} ammonium sulphate solution.

conditions and examining the aqueous phases from each extraction by α-counting. Essentially complete reduction of plutonium^{VI} to plutonium^{IV} occurred on adding 0·3 ml of freshly prepared 10% w/v iron^{II} ammonium sulphate before the first extraction. In the absence of nitrite ion, iron^{II} ion is capable of causing further reduction to inextractable plutonium^{III}. Normally, sufficient nitrite is present in nitric acid to stabilise plutonium^{IV} but occasionally poor extraction efficiencies were found (85–90%) and tentatively attributed to nitrite ion deficiency. In all subsequent analyses an adequate concentration of nitrite ion was ensured by adding 0·15 ml of 1*M* sodium nitrite solution together with the iron^{II} solution.

The most favourable acidity for extracting plutonium^{IV} from uranium-rich solutions is dependent upon the uranium concentration as illustrated in Table II. Throughout this work samples were adjusted to 2*M* nitric acid at 100–120 mg/ml of uranium by appropriate nitric acid addition. Some uranium is co-extracted with the plutonium but one wash of the solvent with 4*M* nitric acid reduces the uranium contamination of the solvent to an acceptable level; it also improves decontamination from fission product $\beta\gamma$-activity.

TABLE II. OPTIMUM NITRIC ACID MOLARITY FOR EXTRACTION OF PLUTONIUM^{IV} INTO 1% HYAMINE 1622/BENZENE AS A FUNCTION OF URANIUM CONCENTRATION

Uranium concentration, *mg/ml*	Optimum acidity	Plutonium extracted in a single stage, %
<10	4M	99·6
100	2M	98
300	1M	97

To test the overall performance of the optimised extraction procedure a number of synthetic 2-ml samples, initially 300 mg/ml of uranium, 50–150 μg/ml of plutonium, 3*M* nitric acid and containing added fission product activity, were conditioned with respect to plutonium valency and acidity as described above, then extracted twice with 1% Hyamine 1622 in benzene and the solvent washed once with 2 ml of 4*M* nitric acid. The plutonium contents of the aqueous phases from each extraction and of the 4*M* nitric acid wash were determined by α-counting, correcting for the presence of uranium where necessary. Plutonium losses are shown in Table III from which it is evident that an overall

TABLE III. SUMMARY OF PLUTONIUM LOSSES IN THE EXTRACTION AND WASHING PROCEDURE

Solution	Aqueous after first extraction	Aqueous after two extractions	4*M* nitric acid wash
Initial plutonium, %	1·5–2·0	<0·1	0·15–0·20

efficiency of 99·8% is achieved. The results also emphasise the necessity of the second extraction. The procedure gave decontamination factors of approximately 10^2 for uranium and 10^5 for fission products in agreement with the work of Powell.[10]

Determination of plutonium in the solvent extract

(a) *Evaporation and titration:* The Hyamine 1622 in benzene extract, together with Hyamine 1622 in benzene washings of the extractor, was transferred to the titration cell (Fig. 3) and the benzene removed by careful evaporation. Mechanical losses of up to 5% of the plutonium occurred when attempts were made to evaporate the entire volume (about 6 ml) at a single stage. Exhaustive trials using standard plutonium solutions showed that no loss of plutonium occurred when aliquots of about 1·5 ml were successively evaporated with gentle air stirring. Careful control of the heating was necessary to prevent charring of the non-volatile Hyamine 1622, an effect which causes undesirable masking of the end-point colour in the final titration.

After allowing the residue to cool, 0·05 ml of 4*M* nitric acid was added (to inhibit the formation of polymeric plutonium^{IV} species which do not react with EDTA) and the whole dissolved in acetone. A known volume of 0·01*M* EDTA, in excess over the plutonium to be determined, was added, the solution buffered to pH 4·75 with ammonium acetate/acetic acid solution and sufficient further acetone added to yield a clear solution, followed by a fixed volume of 0·04 w/v % of dithizone. The volume of indicator added must be maintained constant[16] and for the most precise results the volume of buffer solution and acetone must also be controlled. The residual uncomplexed EDTA was titrated using 0·004*M* zinc chloride solution, the green to pink end-point change being followed photometrically and the end-point taken as the point of inflexion of the graph of galvanometer reading against titre.

During the titration the tip of the microburette delivering the zinc chloride solution dipped just below the surface of the solution and to limit diffusion of Hyamine 1622 into the burette the aperture of the tip was reduced to approximately 0·006 inch. For the same reason, and to prevent gradual build-up of foam inside the microburette, the latter was completely emptied and refilled with fresh zinc chloride solution after each titration.

(b) *The blank titre:* A blank titre can arise from three sources, benzene, Hyamine 1622 and uranium co-extracted with the plutonium. The magnitude of the effect for the appropriate quantities of benzene and Hyamine 1622 is shown in Table IV. This compares the blank values with standardisation titres of zinc chloride against the normal volume of EDTA used per determination, benzene, Hyamine 1622 and uranium all being absent. Table IV, in which each figure is the mean of several determinations, indicates that double distillation of the benzene (Analytical Grade) sufficed to eliminate any effect from it. The Hyamine 1622 contribution could not be reduced, even by exhaustive washing with EDTA. Nevertheless the blank titre caused by 60 mg of Hyamine 1622 (the amount used per determination) is seen to be only 1% of the total standardisation titre.

TABLE IV. CONTRIBUTION OF REAGENTS TO THE BLANK TITRE

Conditions	Hyamine and benzene absent	6 ml of benzene present		6 ml of hyamine 1622/ benzene present		60 mg of hyamine present
		As received	Twice distilled	Benzene as received	Benzene twice distilled	
Titre (microburette units)*	15·00	14·84	14·98	14·70	14·85	14·86

* 1 microburette unit = 0·020 ml.

To assess the blank contribution from uranium, sample analyses were simulated in the absence of plutonium by taking 2 ml of a solution of 3*M* nitric acid containing 300 mg/ml of uranium through the complete extraction, evaporation and titration procedure. Typical titres so obtained, which represent the total blank from benzene, Hyamine 1622 and uranium, are given in Table V, and comparison with Table IV shows the uranium contribution to be approximately equal to that from Hyamine 1622.

TABLE V. DETERMINATIONS OF TOTAL BLANK TITRE (REAGENTS + URANIUM)

	Laboratory solutions of uranium in nitric acid							Process plant solution after removal of plutonium				
Standardisation titre (microburette units)	15·10	15·05	15·10	15·12	15·10	15·10	15·10	15·03	15·05	15·02	15·10	15·01
Blank titre (microburette units)	14·76	14·75	14·80	14·84	14·83	14·80	14·78	14·71	14·75	14·64	14·74	14·62
Difference	0·34	0·30	0·30	0·28	0·27	0·30	0·32	0·32	0·30	0·38	0·36	0·39

Under the extraction conditions described some 5 to 6 mg of uranium enters the titration cell and since further experiments showed that the uranium blank was constant within the limit of experimental error over the range of 3 to 15 mg of uranium it is evident that this is not a source of bias in the method.

Further independent checks on the uranium blank (the constancy of which is difficult to explain) were performed by extracting process plant sample solutions with Hyamine 1622/benzene to remove plutonium, then submitting the uranium-bearing aqueous phase to the full extraction and titration procedure. The results obtained are also shown in Table V, and are seen to be in good agreement with those from laboratory uranium solutions.

Interferences

The Hyamine 1622 in benzene extractant is almost completely selective for plutonium and the method suffers little interference from foreign ions. Only those ions which co-extract with plutonium and react with EDTA or affect the end-point will give rise to interference. Foreign ions may be present as impurities in the reagents used and in the uranium, or as fission products and transuranic elements formed during irradiation of the uranium.

Reagent impurities are compensated for in the blank titration, where, as stated above, the only contribution observed is from the Hyamine 1622. Impurities in the uranium should be similarly accounted for, but since their level may vary from one source of uranium to another the effect of several commonly occurring impurities has been examined. Chromium and nickel do not interfere up to the 0·5 mg/ml level, which exceeds the impurity variation normally anticipated.

Fission product elements were examined collectively by making up a non-radioactive solution approximately simulating normal sample conditions and taking a number of 2-ml aliquots through the entire procedure. This solution, which had the following composition:

Element	Sr	Zr	Mo	Ru	Cs	La	Ba	Ce
Concn., *μg/ml*	5	15	12	7	15	25	5	10

produced no interference in either blank or plutonium titrations. A further solution was then prepared containing each element at a concentration of 1 mg/ml. Two-ml volumes of this solution (which represents fission product levels far in excess of normal circumstances) when subjected to the full procedure yielded a positive interference equivalent to 4 μg of plutonium.

Of the transuranic elements only neptunium-237 is produced in sufficient quantity to interfere. In the presence of the iron^{II} ammonium sulphate conditioner this will be present as neptunium^{IV} which readily extracts into the solvent and will probably interfere quantitatively. The bias so produced is normally much less than 1 % of the plutonium concentration. For accurate work this can be eliminated by performing the method against an external plutonium standard containing an appropriate concentration of neptunium, or with the aid of a correction graph of neptunium concentration against irradiation level.

Certain oxidising agents destroy the dithizone colour by oxidising the indicator to diphenylthiocarbadiazone.[17] Cerium^{IV} is the only such oxidant likely to be present in the sample solutions and this will be reduced to cerium^{III} by the iron^{II} ion conditioner.

Method

(a) *Safety considerations:* The procedure is carried out in a suitably shielded cubicle divided into two sections, a remote-handling section for the solvent extraction of the highly $\beta\gamma$-active sample and a semi-remote unit for the subsequent evaporation and titration of the extract, which is only slightly radioactive.

(b) *Standardisation:* To the clean, dry titration cell, arranged as in Fig. 2, add 2 ml of acetone and 1 ml of buffer solution. From an Agla microburette add an accurately measured volume (about 0·12 ml) of 0·01*M* EDTA solution, washing the tip of the microburette with a few drops of acetone before withdrawing it. Add 0·15 ml of 0·04 % dithizone solution and titrate the solution with 0·004*M* zinc chloride solution from a second microburette, the tip of which should be immersed just below the surface of the solution. Stir the solution by a gentle flow of air between successive additions of titrant. As the end-point is approached make additions of 0·002 ml and record the galvanometer reading after each addition. Derive the end-point from the point of inflection of the plot of galvanometer reading against the titre. Carry out at least two standardisations to establish the satisfactory functioning of the burettes before commencing the analysis of a batch of samples. Table V shows the order of reproducibility which should be achieved.

(c) *Sample analysis:* Take an aliquot of the sample containing 100–200 μg of plutonium using the remotely controlled pipette (Fig. 4) and transfer it to extractor I of the solvent extraction unit (Fig. 1) using a 3-ml polythene cup as the transfer vessel. By the same means add sufficient dilute nitric acid to yield a final acidity of 2*M* and a uranium concentration between 100 and 150 mg/ml. Mix the contents of the extractor and add 0·3 ml of 10 % iron^{II} ammonium sulphate, 0·15 ml of 1*M* sodium nitrite and

2 ml of 1% Hyamine 1622 in benzene via the polythene cup. Mix the phases for 90 sec, allow them to separate, eject the aqueous layer into a second 3-ml polythene cup and transfer this solution into extractor II. Wash the cup with 2 ml of 1% Hyamine 1622 in benzene solution and draw this into extractor II. Mix the phases and allow to separate as described above and eject the aqueous phase to the radioactive drain. Transfer the solvent in extractor II to extractor I, again using a polythene cup for the transference. Wash extractor II with 2 ml of 4*M* nitric acid and combine this solution with the bulked solvent extracts in extractor I. Mix the phases for 90 sec, allow them to separate, and reject the aqueous layer. A trace of the aqueous phase (about 10 μl) should be left with the solvent because it is essential that recovery of the solvent should be quantitative. Eject the solvent into a 5-ml polythene cup. Wash extractor I with 1 ml of 1% Hyamine 1622 in benzene solution and eject this into a 3-ml polythene cup.

Using a glass tube drawn to a fine capillary bore at one end and with a rubber teat attached to the other, transfer 1 ml of the solvent from the 5-ml cup to the clean, dry titration vessel. Apply the heating current and stir the solution carefully with a gentle stream of air. Transfer the remaining solvent in small volumes, maintaining the volume of solution in the titration vessel at about 1·5 ml. Use the solvent in the 3-ml cup to wash the 5-ml one and finally use 1 ml of fresh solvent to wash both cups and the transfer tube. After the final addition of solvent to the titration cell allow the solution to evaporate to about 0·7 ml, switch off the heating current and remove the final traces of benzene by gentle air stirring. Allow the residue to cool, add 50 μl of 4*M* nitric acid and stir for 1 min. Add 1 ml of acetone followed by the appropriate accurately measured volume (normally 0·12 ml) of 0·01*M* EDTA delivered from a microburette. Stir gently, add 1 ml of ammonium acetate/acetic acid buffer solution (pH 4·75) and acetone to clarify the solution. Add 0·15 ml of 0·04% dithizone solution and titrate the excess of EDTA using 0·004*M* zinc chloride solution according to the "standardisation" procedure.

(d) *Blank determinations:* Take a suitable aliquot of a solution of similar acidity and uranium concentration to the sample and carry this through the operations of section (c) above.

(e) *Calculation of result:* The concentration C of plutonium (μg/ml) of sample solution is given by:

$$C = 1000 \frac{W(v_2 - v_1)}{V} M$$

where v_1 and v_2 are the sample and blank titres (ml) V is the volume of the initial sample aliquot, M the molarity of the zinc chloride solution and W is the atomic weight of plutonium. W is not a fixed quantity since it depends upon the isotopic composition of the plutonium under examination, and this is a function of the irradiation dosage. For work requiring the highest accuracy it is necessary to run the sample analysis against an external plutonium standard of similar isotopic composition.

RESULTS

The accuracy and precision of the method have been extensively tested using both standard plutonium solutions containing a large excess of uranium, and on a homogenised volume of process solution. In the latter case standard additions of plutonium

TABLE VI.—PERFORMANCE OF METHOD ON STANDARD PLUTONIUM SOLUTIONS

Plutonium present in standard, $\mu g/ml$	Plutonium found, $\mu g/ml$	Standard deviation, σ
98·5	98·5, 98·9, 98·2, 98·3 98·2, 98·5, 98·9, 98·4 Mean value = 98·5	0·23%
99·9	100·2, 100·5, 100·3, 99·5 100·8, 99·5, 100·3, 99·5 99·0, 99·6 Mean value = 99·9	0·43%

TABLE VII. PERFORMANCE OF METHOD ON A BULKED PROCESS SOLUTION

Plutonium by Hyamine 1622/EDTA, $\mu g/ml$	Standard Deviation, σ	Plutonium by check method, $\mu g/ml$	Process solution + 98·5 μg of plutonium by Hyamine 1622/EDTA, $\mu g/ml$	Recovery, %
95·0, 95·0, 94·5				
95·5, 95·0, 94·6	0·37%	96·5[a]	194·2	100·6
95·5, 94·9, 95·6		94·8[b]	193·0	99·3
95·1		95·1[b]	193·2	99·5
Mean value = 95·1				

Notes [a] = radiometric method
[b] = absorptiometric method[9]

were made in some instances as a further check on its recovery and check analyses by α-counting and the Hyamine 1622/thoronol absorptiometric method[9] were carried out. Typical results are shown in Tables VI and VII. The method is capable of a standard deviation of 0·3–0·4% with an accuracy of about $\pm$0·3% at the 100-μg plutonium level.

Zusammenfassung—Ein genaue und reproduzierbare Methode zur Bestimmung von Plutonium in einer salpetersauren Lösung der Produkte einer Uraniumbestrahlung ist beschrieben. Pu(IV) wird extrahiert unter Verwendung einer benzolischen Lösung des quaternären Amines, Hyamine 1622. Das Benzol wird durch Verdampfen entfernt; nach Lösen des Verdampfungsrückstandes in Aceton wird EDTA im gemessenen Überschuss zugesetzt und der Überschuss mit zink zurücktitriert. Dithizon dient als Indicator; der Endpunkt wird photometrisch festgestellt. Die Extraktion ist höchselektiv für Pu. In einem zweistufigen Cyklus ist der Decontaminierungsfaktor 10^5 für Fissionsprodukten und 100 für Uran. Unter gut kontrollierten Bedingungen beträgt die Standardabweichung der Methode 0.4% für 100 μg Pu.

Résumé—Les auteurs décrivent une méthode précise de dosage de plutonium dans des solutions dans l'acid nitrique, d'uranium irradié. Le plutonium(IV) est extrait par une amine quaternaire: hyamine 1622 dissoute dans le benzène; le benzène est séparé par évaporation et, après dissolution du résidu dans l'acétone, un excès d'EDTA est ajouté; l'EDTA non complexé est titré par photométrie avec une solution de chlorure de zinc étalon et la dithizone comme indicateur. L'estraction est spécifique du plutonium, et il résulte d'une opération en deux étapes un facteur de décontamination approximativement de 10^5 pour les produits de fission mélangés et de 100 pour l'uranium. Dans des conditions soigneusement controlées, la méthode conduit à un écart standard de 0,4% pour des quantités de 100 μg de plutonium.

REFERENCES

[1] *Analytical Chemistry of the Manhattan Project*, Ed. C. J. Rodden. National Nuclear Energy Series VIII—I, McGraw-Hill, 1950, p. 665.
[2] G. M. Allison, Atomic Energy of Canada Ltd., Report PDB 87.
[3] G. Phillips, *Analyst*, 1958, **83**, 75.
[4] W. N. Carson jun., J. W. Vanderwater and H. S. Gile, *Analyt. Chem.*, 1957, **29**, 1417.
[5] F. A. Scott and R. M. Peekema, *Peaceful Uses of Atomic Energy*, 2nd Conference, Geneva, 1958, Paper 914.
[6] W. D. Shults, Oak Ridge National Laboratory Report ORNL 2776, 1959.
[7] C. F. Metz and G. R. Waterbury, *Analyt. Chem.*, 1959, **31**, 1138.
[8] R. K. Webster, A. A. Smales, D. F. Dance and L. J. Slee, *Analyt. Chim. Acta*, 1961, **24**, 371.
[9] United Kingdom Atomic Energy Authority, Industrial Group, Report IGO-AM/W.115.
[10] R. Powell, *Analyst*, 1958, **83**, 252.
[11] J. K. Foreman and T. D. Smith, *J. Chem. Soc.*, 1957, 1752.
[12] A. D. Gel'man, P. I. Artyukhin and A. I. Moskvin, *Russ. J. Inorg. Chem.*, 1959, **6**, 599.

[13] M. J. Cabell, *Analyst*, 1952, **77**, 859.
[14] G. W. C. Milner and J. L. Woodhead, *ibid.*, 1956, **81**, 427.
[15] H. M. Ockenden and J. K. Foreman, United Kingdom Atomic Energy Authority, Production Group, unpublished report.
[16] E. Wänninen and A. Ringbom, *Analyt. Chim. Acta*, 1955, **12**, 308.
[17] F. J. Welcher, *Organic Analytical Reagents*. Van Nostrand, 1948, Volume III, p. 465.

Talanta, 1962, Vol. 9. pp. 65 to 70. Pergamon Press Ltd. Printed in Northern Ireland

THE REGENERATION OF SPENT MAGNESIUM PERCHLORATE DESICCANT

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Summary—The regeneration of spent magnesium perchlorate is described.

Directions are given for the purification of perchlorate for recovery. Exfoliated vermiculite is employed as carrier base. A description is given of the compounding of a carrier-based granular product by absorption of a saturated aqueous solution of magnesium perchlorate and the dehydration to form a finished product of bulk density 20·5 lb per cu ft. The fraction retained on a 10-mesh sieve and passing through a 5-mesh sieve is approximately 75% anhydrous magnesium perchlorate in a highly dispersed condition.

The testing of carrier-based anhydrous magnesium perchlorate for drying efficiency is described.

GENERAL CONSIDERATIONS

DEHYDRATED magnesium perchlorate for use as a desiccant was first studied by Willard and Smith in 1922.[1] In the form of $Mg(ClO_4)_2 \cdot 3H_2O$ it was proposed as a desiccant for use in organic combustion analyses in the determination of carbon and hydrogen, and for the determination of carbon in steel by combustion in oxygen. Vacuum drying equipment in the manufacture of the anhydrous material, for use in general analytical applications, was described by Smith and Rees.[2] A thorough study of the properties of magnesium perchlorate in the form of its hexa-, tetra-, and dihydrates as well as in the anhydrous granular porous form was made by Smith, Rees and Hardy.[3] Their studies were reprinted in a booklet by Smith[4] which includes a study of the use of anhydrous magnesium perchlorate in the dehydration of air for liquifaction and fractionation to prepare high pressure tank oxygen. For this purpose it was successfully applied[5] for a period of six months in a study of the efficiency attained in plant practice. An increase in plant yield of oxygen and a material saving in power consumption were demonstrated. Anhydrous magnesium perchlorate is now a standard desiccant, commercially available under the trade names *Dehydrite* and *Anhydrone* as well as under its chemical designation. Its use in laboratory desiccators was described by Smith, Bernhart and Wiederkehr.[6] Its use in the preparation of anhydrous perchloric acid, through dehydration of the aqueous acid and vacuum distillation, was described by Smith.[7] The American Chemical Society Reagent Specifications[8] require the maximum water content to be less than 10%. Commercially available "anhydrous" magnesium perchlorate is manufactured to contain approximately 5% of residual water. A rapid test for its water content has been described by Smith.[9]

According to data published by Bower at the U.S. Bureau of Standards,[10] anhydrous magnesium perchlorate would appear to be less efficient in the absorption of water than phosphorus pentoxide. This is, however, incorrect, since it has been shown[3] that phosphorus pentoxide is ineffective in the dehydration of magnesium perchlorate dihydrate to the anhydrous product at any temperature up to over 100°, or, indeed, at any higher temperature at which phosphorus pentoxide may be

effectively employed. An exhaustive study by Diehl and his associates[11] shows that anhydrous magnesium perchlorate leaves in a gas stream only one twentieth of the amount of water left by phosphorus pentoxide at its best performance. The capacity for the absorption and adsorption of water by anhydrous magnesium perchlorate is roughly 35% of the weight of the starting product. An industrial supply of anhydrous magnesium perchlorate has been provided, following a complete description of the operations involved.[4] The dew point of air, dried by anhydrous magnesium perchlorate, is approximately the same as that at the temperature of liquid air.

The statement is often made that a given desiccant is highly efficient but that it may be readily regenerated. Such statements have no justification. The more efficient a desiccant is the more difficult is its regeneration. The object of the present work is to describe a practical method for the regeneration of anhydrous magnesium perchlorate.

One of the most outstanding properties of anhydrous magnesium perchlorate is its high temperature coefficient in the absorption of water vapour. It has been shown to absorb water efficiently at temperatures in excess of 150°. It reacts with ammonia quantitatively to form di-, tetra-, and hexammoniates.[12] Magnesium perchlorate diammoniate retains its absorbed ammonium at temperatures in excess of 175°.

Anhydrous magnesium perchlorate is stable at 290°, at or below which temperature no dissociation with the evolution of oxygen can be observed. It has been prepared in 95% yield by the dry reaction of mixtures of ammonium perchlorate and magnesium oxide heated in vacuo to 250–260°.[13] As a result of the preparation of anhydrous magnesium perchlorate by high vacuum dissociation of its hexahydrate, unaccompanied by fusion, the finished desiccant has an exceptionally high porosity caused by capillary voids. By virtue of this property, alcohol vapours, and a number of other volatile organic vapours, are readily adsorbed quantitatively. This has been employed analytically. It is also of great importance when magnesium perchlorate is used for the dehydration of air in the manufacture of liquid air. The contamination by cracked hydrocarbons from oil lubricated pressure pumps of the air being liquified does not pass into the liquid oxygen of the fractionation column used to separate oxygen from nitrogen. Thus explosion hazards from contact of the oxygen with an accumulation of organic matter are eliminated.

Granular anhydrous magnesium perchlorate, with added colour to indicate its exhaustion as desiccant by a colour change, has been described by Smith.[14] As shown by Nemeth,[15] this has a very valuable advantage when using Pregl tubes for micro carbon and hydrogen determination in organic combustion analyses. This indicating desiccant was prepared at the request of Lieb.

REGENERATION OF SPENT MAGNESIUM PERCHLORATE DESICCANT

Spent magnesium perchlorate desiccant is unsuited for immediate regeneration, since it may be contaminated by impurities such as organic matter which, at the temperatures required, would be objectionably reactive. The first step should be the dissolution of the spent reagent in water, followed by filtration and boiling to volatilise organic impurities. The boiling, which occurs at a temperature of 130–135°, followed by slow cooling, causes the deposition of large crystals of the hexahydrate. The cooled crystals and accompanying saturated aqueous solution are centrifuged to separate off the crystals, and the residual solution is mixed with further solutions which are

then subjected to similar crystallisation processes. The hexahydrate may then be dehydrated in stepwise fashion in electrically heated vacuum ovens to form, successively, the tetrahydrate, then the dihydrate, and finally the anhydrous finished product. These operations must be carried out at predetermined maximum temperatures for each stage of the dehydration as described previously.[4] This process is unsuited to small-scale regeneration of spent desiccant, but has been used by the manufacturers for large-scale regeneration in applications such as that described previously.[5] For small-scale regeneration of spent magnesium perchlorate desiccant a practical procedure involves the addition of a supporting base or carrier. By proper selection of carrier, the recovered reagent can be compounded in granular form to give a product with a high surface of contact which is not dependent upon dehydration without fusion, as is the case when starting with crystals of the hexahydrate.

EXPANDED VERMICULITE AS A GRANULATED DESICCANT CARRIER

Expanded vermiculite, which is a bulk material now commercially available, is sold under various trade names one of which is *Zonolite*. This product is commonly supplied for use as an insulating material for air-conditioning household insulation or for use as aggregate in the compounding of light weight "concrete" in combination with cement and other ingredients. Another extensive use of expanded vermiculite is as absorbent packing material for transportation of corrosive liquids in glass; the packing material serves as cushioning material to protect against breakage with rough handling or to serve as a non-reacting absorbent in case of breakage of containers in transit. Expanded vermiculite has a bulk density of approximately 6·5 lb per cu ft. The average analysis of seven different samples of mined vermiculite is given in Table I.

Vermiculite occurs in broad crystals or crystalline flakes with a yellowish-brown, greenish-black, or greenish-yellow colour. It has a soapy graphitic feel. Deposits of vermiculite are found in many parts of the world. The American deposits are located in Montana, Colorado, and Wyoming. At 110°, with gradual heating, half of the water content is expelled without distortion of the original physical conglomerate.

TABLE 1. AVERAGE ANALYSIS OF SEVEN NATURALLY OCCURRING VERMICULITES, SP.GR.APP. 2·13.

Unit Cell—4 Moles-$[(OH)_2(Mg,Fe)_3(Si,Al,Fe)_4O_{10}\cdot 4H_2O]$

	Analysis, %	Theoretical	Composition
SiO_2	35·04	36·71	22 SiO_2
Al_2O_3	14·55	14·15	5 Al_2O_3
Fe_2O_3	5·13	4·43	Fe_2O_3
FeO	0·59		
NiO	2·44		
MgO	21·71	24·62	22 MgO
CaO	0·46		
H_2O	19·99	20·09	40 H_2O

Average Formula: 22 MgO·5 Al_2O_3·Fe_2O_3·22 SiO_2·40 H_2O

EXFOLIATION OF VERMICULITE AT 1000–1100°

The most outstanding properties of vermiculite are its exfoliation when exposed to elevated temperatures and its chemical inertness in the heat-expanded form. The

surface of a sample of vermiculite, as mined, was measured by Brunauer, Emmett, and Teller[16] by nitrogen adsorption at −195°, and was found to be 0·52 m^2 per g. The platelet thickness calculated from this is 1·8 μ when the theoretical density of 2·13 is assumed. This indicates that vermiculite is extensively fissured before exfoliation. The same sample of vermiculite was exfoliated by heating for 5 min at 950°. There resulted a silvery-white accordion-like structure, and the change was associated with a loss in weight of 19·6%. The surface area of the exfoliated sample was 10·35 m^2 per g, and the calculated platelet thickness was 0·091 μ.

Vermiculite consists of sheets of magnesium aluminum silicate of 9·26 Å thickness with alternate layers of 8 H_2O spaced at about 4·8 Å.[17] The exfoliated vermiculite has platelets 200 times this thickness; Gruner[17] suggests that this is because of structure collapse above 750°, and that it indicates that exfoliation is a mechanical process consequent on the formation of steam.

It is claimed that a modified procedure for exfoliation[18] produces a much greater surface.

PREPARATION OF EXPANDED VERMICULITE AS CARRIER-BASE MATERIAL

Expanded vermiculite, as supplied to the building trade, is granular, with a maximum particle size of 10–12 mm. This material is sifted to any suitable intermediate granular size and is ready for impregnation. A particle size passing 5-mesh and retained on a 10-mesh screen* is appropriate for use in the process described below.

IMPREGNATION OF EXPANDED VERMICULITE WITH AQUEOUS MAGNESIUM PERCHLORATE AND DEHYDRATION

The saturated aqueous solution of magnesium perchlorate recovered as described above, and at ordinary temperature, is placed in a large vacuum desiccator. The vermiculite carrier, contained in a wire basket with a wire screen closure at the top, is completely immersed in the perchlorate solution. Vacuum is then applied followed by release to ordinary pressure, and this operation is repeated a number of times. By this procedure the carrier absorbs the maximum amount of the hydrated desiccant and excess solvent. Upon removal from the saturating solution, the product is allowed to drain for a few min and is then ready for dehydration to carrier-based anhydrous magnesium perchlorate desiccant. The material thus formed does not "weep", either in the original saturated form or during the subsequent dehydration.

An electric muffle furnace is suitable for the dehydration. The impregnated carrier-based product is spread on trays made of nichrome gauze or a substitute material to a depth of 1–2 cm. Wire mesh trays with 2–3-cm sides, which stack one upon the other leaving ample space between the layers of material to be dehydrated, are used. The muffle furnace should be set to give a maximum temperature of 230 to 250°. The product can be placed in the muffle at this temperature. No bleeding of the carrier granules will result. Drying under atmospheric pressure is continued for 24–48 hr or to constant weight of the finished product. (For the commercial preparation of carrier-based anhydrous magnesium perchlorate, specially constructed high-vacuum drying ovens are used.)

* This sifted product constitutes approximately 35–45% by weight of a starting material which is commercially available at $0·50–0·60 per cu ft.

PHYSICAL CONSTANTS OF CARRIER-BASED ANHYDROUS MAGNESIUM PERCHLORATE

The physical constants of the desiccant prepared as described are as follows:

Bulk density: 328 g per 1000 ml or 9287 g (20·5 lb) per cu ft.

Carrier weight: 23·75% or 4·86 lb per cu ft.

Anhydrous magnesium perchlorate: 76·25% or 15·62 lb per cu ft.

TESTING OF DRYING EFFICIENCY AND CAPACITY

A cylindrical drying tower constructed of stainless steel, 200 mm (8 in.) in diameter and 600 mm (24 in.) high, was employed. This was fitted with a tube passing from the top to the bottom for the admission of moist air, a pressure gauge of range 0–100 psi, and a discharge vent at the top with needle-valve control. The total volume was 19,060 ml (0·673 cu ft.). The air intake was connected to the laboratory compressed air line through an open valve. The pressure in the drying tower ranged from 60 to 68 psi, and was mostly, during the off-peak load demand, at the higher pressure. The air supply was saturated with water vapour at the ambient temperature and the pressure prevailing.

The rate of flow of gas from the drying power was measured by a standard wet-test meter and was adjusted to 1 cu ft (28317 ml) per min, continuously operated.

The effluent line was sampled at 24-hr intervals. A Pregl micro-combustion absorption tube charged with anhydrous granular Indicator Anhydrone[14] was used for this operation. The rate of gas flow through the Pregl tube was approximately 150 ml per min, and 5000 ml of withdrawn dehydrated air was passed for each test to determine drying efficiency. The performance of this test for 12 consecutive days is shown in Fig. 1.

EFFICIENCY OF DEHYDRATION

Fig. 1 shows that after the passage of more than 10,000 cu ft of air the complete removal of water was attained over a period of 7 days. By direct determination each

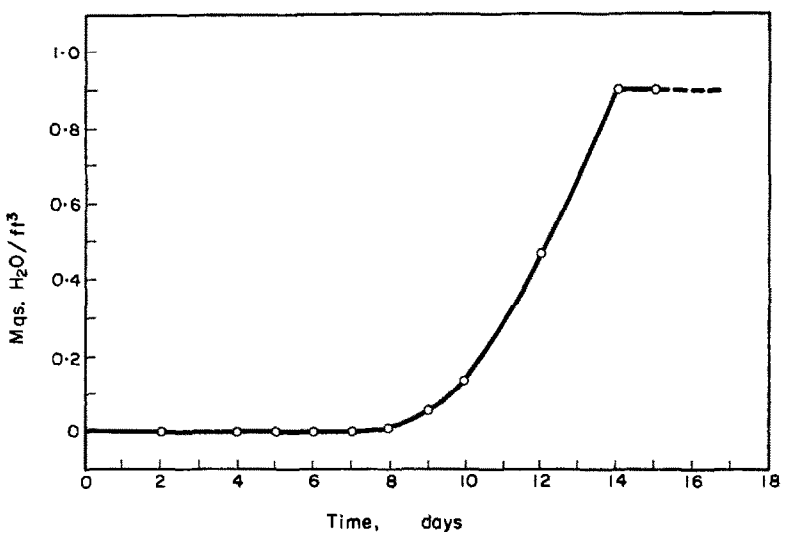


FIG. 1

cu ft of dried air contained 0·1507 g of water vapour or 3·548 lb of water in 10,000 cu ft. The carrier-based anhydrous magnesium perchlorate in the 8 × 24 inch absorption tower weighed 13·8 lb. Therefore the capacity of the desiccant for perfect absorption of water under the conditions described was 25·71% of the original weight of desiccant. The anhydrous magnesium perchlorate content of the carrier-based desiccant was 10·32 lb. Thus the perchlorate desiccant adsorbed 34·4% of its weight, which corresponds to the capacity of granular, porous anhydrous magnesium perchlorate employed without added carrier-base. The second stage of dehydration efficiency involves the absorption of water by conversion of $Mg(ClO_4)\cdot 2H_2O$ to the tetrahydrate. The absorption of water at this stage is inefficient to the extent of 0·85 mg per litre of air dried, or approximately 16 mg per cu ft.

Zusammenfassung—Die Regenerierung von verbrauchtem Magnesiumperchlorat wird beschrieben. Anweisung zur Reinigung des Perchlorates werden mitgeteilt. Vermiculit wird als Träger verwendet. Magnesiumperchlorat wird als gesättigte, wässrige Lösung auf den Träger gebracht; nach Dehydratation erhält man ein granuliertes Endprodukt. Die Schüttdichte des Produktes is 20.5 Pfund per Kubikfuss. Die Teilchengrösse entspricht 75% zwischen 10-Maschensieb und 5-Maschensieb. Die Wirksamkeit des auf dem Träger befindlichen Perchlorates wurde überprüft und als zufriedenstellend gefunden.

Résumé—L'auteur décrit la régénération de perchlorate de magnésium. Des directives pour la purification du perchlorate à récupérer sont données. La vermiculite exfoliée est utilisée comme entraineur. La combinaison de l'entraîneur à base de produit granulaire par absorption d'une solution aqueuse saturée de perchlorate de magnésium et la déshydratation pour former le produit final sont décrites. On obtient ainsi un produit fini de densité: 20,5 livres par pied cubique. Le produit fini de dimension particulaire, retenu sur un tamis de 10 mesh et passant à travers un tamis de 5 mesh, contient approximativement 75% de perchlorate de magnesium anhydre sous forme très dispersée. Le pouvoir desséchant du perchlorate de magnésium anhydre est contrôlé.

REFERENCES

[1] H. H. Willard and G. Frederick Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 2255.
[2] G. Frederick Smith and O. W. Rees, *Ind. Eng. Chem.*, 1931, **23**, 1328.
[3] G. Frederick Smith, O. W. Rees and V. R. Hardy, *J. Amer. Chem. Soc.*, 1932, **54**, 3513.
[4] *Dehydration Studies Using Anhydrous Magnesium Perchlorate.* G. Frederick Smith Chemical Company, Columbus, Ohio, 1935, p. 59.
[5] G. Frederick Smith, *Chem. and Ind.*, 1934, 357.
[6] G. Frederick Smith, D. N. Bernhart and V. R. Wiederkehr, *Analyt. Chim. Acta*, 1952, **42**, 6.
[7] G. Frederick Smith, *Talanta*, 1961, **7**, 212.
[8] *Reagent Chemicals.* American Chemical Society Specifications, 1950.
[9] G. Frederick Smith, *Talanta*, 1960, **5**, 189.
[10] V. E. Bower, *Bur. Stand. J. Res.*, 1933, **12**, 46.
[11] Harvey Diehl, private correspondence.
[12] G. Frederick Smith and E. G. Koch, *Z. anorg. Chem.*, 1935, **223**, 17.
[13] G. Frederick Smith and V. R. Hardy, *ibid.*, 1935, **223**, 1.
[14] G. Frederick Smith, *Talanta*, 1959, **3**, 107.
[15] Joseph Nemeth, micro-Analyst, University of Illinois, private communication.
[16] S. Brunauer, P. H. Emmett and E. Teller, *J. Amer. Chem. Soc.*, 1938, **60**, 309.
[17] J. W. Gruner, *Amer. Mineral.*, 1934, **19**, 557.
[18] C. S. Miner, *U.S. Patent* 1, 922, 448, 1934.

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PRELIMINARY COMMUNICATIONS

Selective chelatometry of copper^{II} with ethylenediamine-*N,N,N′,N′*-tetra-n-propionic acid

(*Received* 26 *October* 1961)

IN a recent review of some aspects of the selectivity of chelatometric titrations it has been indicated that, without recourse to auxiliary complexing agents, selectivity of titration with reagents of the complexan group is only possible by the simultaneous availability of selective chelating agent *and* selective pM indicator.[1] In the same paper, the high selectivity of ethylenediamine-*N,N,N′,N′*-tetra-n-propionic acid, referred to subsequently as EDTP, and the -*N,N′*-di-n-propionic acid (EDDP) towards copper^{II} ion[2] was stressed. The strength of the copper^{II} chelates of these reagents relative to their chelates with magnesium, cadmium, *etc.* was attributed to the (relatively) uncommon square-coplanar habit of the copper^{II} ion and the presence in both reagents of the $\diagdown\!\!\diagup N—CH_2—CH_2—N\diagdown\!\!\diagup$ chain. The replacement of acetic acid groups (EDTA) by n-propionic acid groups critically weakens the strength of the primary chelate ring for most metal ions and results in low stability constants for the EDTP and EDDP chelates of magnesium ($10^{1.8}$, $10^{1.6}$), cadmium ($10^{6.0}$, $10^{5.6}$), *etc.*,[2] whereas the steric disposition of the copper^{II} bonding and its well known tendency to react well with molecules containing $\diagdown\!\!\diagup N—CH_2—CH_2—N\diagdown\!\!\diagup$ groups ensures efficient chelation of copper ($10^{15.4}$ $10^{15.1}$).

The above findings suggested to us that these reagents should serve as useful titrants for copper^{II} in the presence of several other ions; but such a reagent is of no avail with conventional metallochromic indicators since these will respond to the presence of other metal ions such as magnesium, *etc.* However, two virtually specific indicators for copper^{II} have been described previously *viz.* Fast Sulphon Black F[3] and Ponceau 3R.[4] The first of these indicators responds only to copper^{II} and nickel and the second also to copper and nickel. In both cases the quality of the nickel end-point is poor.

In our preliminary experiments, of which this communication is a brief report, the EDTP/Ponceau 3R system was explored using $10^{-2}M$ solutions of copper^{II}, other metals and the complexan. The titrations were carried out using an Agla micrometer syringe burette, with a total volume of titration medium of approximately 1 ml. Ponceau 3R works most effectively at pH $\approx$ 9 in an ammoniacal medium, when the colour change is from yellow to red. The quality of the end-point in the EDTP titration of copper^{II} is only slightly inferior to that with the considerably stronger complexan EDTA. Interference studies were carried out with *ca.* 60 μg of copper^{II} and varying concentrations of magnesium, calcium, barium, strontium, cadmium, manganese, zinc, lead, cobalt, nickel and aluminium. When EDTA was used as titrant all of these titrated additively with the copper. With EDTP, however, no interference was found from 10 molar ratios of magnesium or calcium or from 5 molar ratios of strontium, barium and cadmium. No attempt was made to find the upper limit of non-interference of these five ions. Manganese^{II} did not interfere up to a 2 molar ratio, but larger amounts promoted sluggish end-points and low copper recoveries, presumably caused by coprecipitation of some copper with manganese hydroxide. Cobalt interfered, of course, by virtue of its colour and zinc and lead could not be held in solution at pH 9. A slight raising of the pH to 10 allowed the titration of copper in the presence of a 1 molar ratio of zinc, though the quality of the end-point was considerably impaired at this pH. Nickel titrated as copper with a sluggish end-point while aluminium could be maintained harmlessly in solution by the addition of fluoride ion.

The procedure was applied successfully to the small-scale analysis of copper in a standard brass sample (70.8% of Cu, 24.17% of Zn, 1.85% of Sn, 2.52% of Pb, 0.31% of Fe, 0.12% of Mn, 0.17% of Ni). The brass was dissolved in the usual way, the solution diluted, the pH adjusted to 9-10 and the copper titrated directly with EDTP without significant interference from the other elements present.

Further more detailed experiments will shortly be initiated with Fast Sulphon Black F[3] as indicator. This indicator functions at pH $\approx$ 11 where aluminium, lead, zinc, *etc.* can be held in solution. The indicator action of Ponceau 3R is rather dependent on electrolyte concentrations and pH; but it was used in these preliminary small-scale experiments because it is rather more sensitive.

EXPERIMENTAL

Reagents

$10^{-2}M$ *EDTP:* Prepared by condensation of 3-chloro-n-propionic acid with ethylenediamine.
$10^{-2}M$ $CuSO_4$: Standardised against EDTA.
Indicator: 0.25% aqueous Ponceau 3R.
Buffer: 54 g of NH_4Cl plus 22 ml of NH_3 solution (sp. gr. 0.88), diluted to 1 litre.

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Summary—A highly selective complexometric titration of copper[II] is reported using the complexan ethylenediamine-*N,N,N',N'*-tetra-n-propionic acid and a selective metallochromic indicator.

Zusammenfassung—Es wird eine Methode fur eine hoch-selektive complexometrische Titrierung von Kupfer(II) mittels. Athylendiamin-*N,N'*-tetra-n-propionsaüre und ein selektives metallochromisches Indikator angelgeben.

Résumé—On décrit une méthode complexométrique pour le dosage de cuivre (II) par l'acide ethylénediamine-*N,N,N',N'*-tétra-n-propionique avec un indicateur métallochromique.

REFERENCES

[1] T. S. West, *Analyt. Chim. Acta*, 1961, **25**, 301.
[2] R. C. Courtney, S. Chaberek and A. E. Martell, *J. Amer. Chem. Soc.*, 1953, **75**, 4814.
[3] R. Belcher, R. A. Close and T. S. West, *Chem. and Ind.*, 1957, 1647.
[4] *Idem, Chemist-Analyst*, 1957, **46**, 86.

Analytical aspects of the oxidation of organic nitrogen compounds with chromic acid

(*Received* 4 *September* 1961.)

THE oxidation of a series of organic nitrogen compounds from different classes with chromic acid in a medium of dilute sulphuric acid has been systematically investigated. From the consumption of the oxidising agent, oxidation numbers have been calculated and defined as the amount of oxygen in grams consumed by the oxidation of 100 grams of the substance. The oxidation numbers calculated from the experimental data have been compared with the theoretical ones that had been calculated from the oxidation equations for the tested compounds. In most cases a good agreement was found, the following processes being taken into consideration:

Carbon and hydrogen are oxidised to carbon dioxide and water, respectively, nitro and nitroso groups (attached to carbon, nitrogen or oxygen) being oxidised to nitric acid; two nitrogen atoms attached to each other as in azo compounds, hydrazines, pyrazoles, *etc.*, are split off in the form of elementary nitrogen and aromatic amino groups are converted into ammonia. From halogen compounds, chlorine and bromine are liberated in the form of the elements, while iodine is oxidised to iodic acid. All groups containing sulphur are ultimately oxidised to sulphuric acid.

The procedure was applied successfully to the small-scale analysis of copper in a standard brass sample (70.8% of Cu, 24.17% of Zn, 1.85% of Sn, 2.52% of Pb, 0.31% of Fe, 0.12% of Mn, 0.17% of Ni). The brass was dissolved in the usual way, the solution diluted, the pH adjusted to 9-10 and the copper titrated directly with EDTP without significant interference from the other elements present.

Further more detailed experiments will shortly be initiated with Fast Sulphon Black F[3] as indicator. This indicator functions at pH $\approx$ 11 where aluminium, lead, zinc, *etc.* can be held in solution. The indicator action of Ponceau 3R is rather dependent on electrolyte concentrations and pH; but it was used in these preliminary small-scale experiments because it is rather more sensitive.

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REFERENCES

[1] T. S. West, *Analyt. Chim. Acta*, 1961, **25**, 301.
[2] R. C. Courtney, S. Chaberek and A. E. Martell, *J. Amer. Chem. Soc.*, 1953, **75**, 4814.
[3] R. Belcher, R. A. Close and T. S. West, *Chem. and Ind.*, 1957, 1647.
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Carbon and hydrogen are oxidised to carbon dioxide and water, respectively, nitro and nitroso groups (attached to carbon, nitrogen or oxygen) being oxidised to nitric acid; two nitrogen atoms attached to each other as in azo compounds, hydrazines, pyrazoles, *etc.*, are split off in the form of elementary nitrogen and aromatic amino groups are converted into ammonia. From halogen compounds, chlorine and bromine are liberated in the form of the elements, while iodine is oxidised to iodic acid. All groups containing sulphur are ultimately oxidised to sulphuric acid.

The oxidation numbers of oximes were, however, lower or higher than the theoretical values when considering the quantitative conversion of the isonitroso group into nitric acid or, alternatively, elementary nitrogen. Amino groups containing one or two methyl groups attached to nitrogen gave lower oxidation numbers than would be expected in the case of quantitative formation of ammonia. This is apparently caused by the partial splitting off of nitrogen as methylamine or dimethylamine, which are relatively stable to the oxidising agent. The oxidation number of a nitrogen compound, however, in connection with its molecular formula, may provide the first information of the nature of the nitrogen functional groups present in the substance under investigation.

Because of the different behaviour of various nitrogen functional groups to chromic acid, new semimicro methods for the selective determination of some forms of nitrogen in organic compounds either separated or combined have been worked out. The elementary nitrogen, split off during the heating of the reaction mixture from groups containing the N—N bond, is collected and measured in a nitrometer. After reducing the chromic acid with iron^{II} sulphate and rendering the reaction mixture alkaline, the ammonia, formed from most types of amino groups, is distilled off and titrated in the usual way. Methylamine or dimethylamine, originating from N-methyl groups which may be present, are distilled off and titrated together with ammonia. The nitric acid formed from the nitro or nitroso groups is then reduced in an alkaline medium with Devarda's alloy to ammonia, which is determined as mentioned above.

The selective determination of various forms of nitrogen and their ratio to the total nitrogen may be of considerable importance for solving problems of constitution.

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Summary—The oxidation of a series of organic nitrogen compounds of different types with chromic acid in dilute sulphuric acid has been examined. The method can provide useful information about the nature of the compound.

Zusammenfassung—Die mit Chromsäure in verdunnte Schwefelsäure Oxydation einer Reihe von organischen Stickstoff-verbindungen underen Arten wird untersucht. Die methode befert wertvolle Auskunft über der Natur der Verbindung.

Résumé—On a examiné l'oxydation d'une série de composés organiques d'azote de types divers, utilisant l'acide chromique dans l'acide sulfurique dilué. Cethe méthode fournit des indications utiles sur la nature des composés.

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SHORT COMMUNICATIONS

Coulometric titration by electrogenerated tin^{II} ion

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THE electrogenerated reducing agents titanium^{III},[1] iron^{II},[2] chromium^{II},[3] uranium^{IV} [4] and copper^{I} [5] have been used for the application of the coulometric titration in chemical analysis. Strong reducing agents have low standard oxidation-reduction potentials, so that the electrolytic generation of hydrogen takes place easily on the surface of the cathode, favouring the use of the less versatile mercury cathode of large hydrogen over-potential rather than a solid cathode. Although tin^{II} ion has long been known as a reducing reagent in conventional titrations, it is very unstable to the action of oxygen in air or water and therefore needs to be stored in the absence of air and restandarised each time it is used. This defect may be overcome by using electrogenerated tin^{II} ion in a coulometric titration. The standard oxidation-reduction potential of tin^{II} ion is +0·05 V *vs.* N.H.E. and its reducing power is weaker than that of titanium^{III} or of chromium^{II}, but stronger than that of iron^{II} or of ferrocyanide.

During the course of the present study, Bard and Lingane[6] published a coulometric titration method using tin^{II}. According to their work, from the standpoint of the current efficiency bromide solution is more favourable than chloride solution as a supporting electrolyte and also a gold electrode or platinum electrode with tin oxide film on its surface gives about 100% current efficiency.

EXPERIMENTAL

Apparatus and reagents

A constant current source, titration cell, potentiometer for end-point detection, time measuring apparatus and stirrer form the coulometric apparatus.[7] The present titration was carried out in a current of nitrogen gas, because tin^{II} ion is readily oxidised in air.

All of the reagents were of commercial special grade, and water was purified by ion-exchange, then boiled and cooled. Nitrogen was purified by passing it through pyrogallol-sodium hydroxide solution followed by water.

DISCUSSION AND RESULTS

The current efficiency was investigated at various compositions of the electrolytic solution by titrating cerium^{IV} sulphate solution with electrogenerated tin^{II} ion. In the electrolyte solution, hydrochloric acid, sulphuric acid, potassium chloride solution as well as hydrochloric acid-potassium chloride solution were employed. Tin^{IV} chloride was dissolved to give a 0·2*M* solution. The generating cathode was a platinum plate (2 × 2 cm^2). In the coulometric titration of 0·01*N* cerium^{IV} sulphate solution at a current of 5 mA, only potassium chloride solution could be used, because at the concentrations employed with the other electrolytes hydrogen gas was evolved on the surface of the generating cathode, resulting in markedly low current efficiencies. Further, the hydrogen gas absorbed on the surface of the indicating platinum electrode disturbs the potential indicator system. The evolution of hydrogen gas increased with the concentration of acid. On the contrary, it was observed that the electrolytic solution became turbid or produced a white precipitate instantaneously or sometimes when tin^{IV} chloride was dissolved in hydrochloric acid ($<0{\cdot}1N$), sulphuric acid ($<0{\cdot}6N$) or potassium chloride solution ($<0{\cdot}2M$).

In the following experiment, 3*M* potassium chloride, ammonium chloride or 3*N* hydrochloric acid was employed for the electrolyte solution. The results are summarised in Table I. According to Table I, potassium chloride solution gives the highest current efficiency. The results obtained at an electrolytic current of 5 mA indicated current efficiencies which were, respectively, about 80% and 60% in ammonum chloride solution and hydrochloric acid.

TABLE I. COULOMETRIC TITRATION OF CERIUM^{IV} BY ELECTROGENERATED TIN^{II} IN VARIOUS ELECTROLYTIC SOLUTIONS

Electrolyte solution	Ce^{IV} taken, *mequiv.*	Electrolytic current, *mA*	No. of expt.	Electrolytic time, *sec*	Std. devn., *sec*
3*M* KCl	0.01824	10.005	5	187·5	1·83
3*M* KCl	0·03648	9·975	5	372·3	3·90
3*M* NH_4Cl	0·01824	10·000	4	200·7	2·07
3*N* HCl	0·01824	9·986	3	417·4	58·2

Although the current efficiency for 3*M* potassium chloride solution does not exceed 95%, the standard deviation is about 1%, so that 3*M* potassium chloride solution can be employed as an electrolyte for tin^{II} coulometry.

Next, the effect of the concentration of tin^{IV} on the current efficiency was examined. The electrolytic solution was composed of 0·5, 0·3, 0·2, 0·1, 0·05 or 0·015*M* tin^{IV} chloride and 3*M* potassium chloride solution. One ml of 0·015*N* cerium^{IV} sulphate solution was titrated with electrogenerated tin^{II} at a current of 5 mA. The current efficiency increases with the concentration of tin^{IV} chloride up to 0·2*M* when it reaches a maximum of 94 ~ 96%.

The effect of the concentration of potassium chloride was then studied. The coulometric titrations of 1 ml of 0·015*N* cerium^{IV} sulphate were carried out with electrogenerated tin^{II} at a current of 5 mA in potassium chloride solutions of concentrations varying from 0·2 to 3*M*. The current efficiency is not less than 95% above a concentration of 2*M* potassium chloride, but falls off below this concentration of potassium chloride.

Summarising the results obtained, the mixture of 0·3*M* tin^{IV} chloride and 3*M* potassium chloride is considered to be the most suitable for the present coulometric titration. Cerium^{IV} ion, free iodine and bromine can be reduced instantly and quantitatively by tin^{II} ion, so that the tin^{II} coulometric titration method can be applied to the determination of these substances. One hundred ml of 0·3*M* tin^{IV} chloride and 3*M* potassium chloride solution were employed, tin^{II} being electrogenerated at a

TABLE II. COULOMETRIC TITRATION OF CERIUM^{IV}, BROMINE AND IODINE

Sample taken, *mequiv.* ($\times 10^{-2}$)	Electrolytic current, *mA*	No. of expts.	Electrolytic time, sec	Sample found, *mequiv.* ($\times 10^{-2}$)	Error, %
Ce^{IV} 0·814	5·097	2	156·3	0·829	2·0
Ce^{IV} 1·628	5·096	2	318·6	1·683	2·4
Ce^{IV} 2·452	5·099	2	485·4	2·565	4·6
Ce^{IV} 4·070	10·076	4	412·2	4·302	5·8
Ce^{IV} 8·140	10·094	4	820·8	8·586	5·5
Ce^{IV} 21·275	14·707	2	1428·4	21·771	2·1
Iodine 2·084	10·055	5	212·4	2·217	6·4
Iodine 5·210	10·055	3	523·1	5.446	4·5
Iodine 20·84	10·160	3	2039·5	21·309	2·3
Bromine 1·010	10·036	5	104·4	1.085	7·4
Bromine 2·020	10·030	5	206·6	2·147	6·3
Bromine 5·050	10·046	4	511·7	5·327	5·5
Bromine 10·10	10·030	4	997·0	10·359	2·6
Bromine 20·20	10·030	3	1963·3	20·559	1·8

current of 10 mA. After passing nitrogen gas through the solution for about 10 min to remove the dissolved oxygen, the sample solution was introduced, then titration commenced in the nitrogen atmosphere. The end-point was detected either potentiometrically or amperometrically. In Table II,

the coulometric titration of cerium^{IV} ion and iodine used the potentiometric method and that of bromine used the amperometric method. In the amperometric detection, the indicating current was expressed with the voltage drop measured through the definite resistance, when the voltage 0·3 ~ 0·4 V was applied between the two platinum electrodes through 100 kΩ resistance.

In conclusion, the coulometric method with tin^{II} ion is considered to be more versatile using a solid electrode such as platinum than that with titanium^{III} or chromium^{II} ions in which cases the mercury electrode is forced to be employed in place of the solid electrode.

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Summary—The coulometric method of electrogenerated tin^{II} ion using the platinum electrode as a generating cathode has been investigated. The electrolytic solution comprising 3*M* potassium chloride and 0·3*M* tin^{IV} chloride has been found to be satisfactory for the determination of cerium^{IV} ion, iodine and bromine with an error of only a few percent provided suitable conditions are employed.

Zusammenfassung—Coulometrie mit Zinn(II)-ionen (an einer Platinelektrode erzeugt) wurde untersucht. Eine elektrolyt welcher 3M in Kaliumchlorid und 0,3M in Stannichlorid ist wurde für die Titration von Cer(IV), Jod und Brom geeignet gefunden.

Résumé—Les auteurs ont étudié la coulométrie à l'aide de l'ion stanneux préparé par électrolyse, en utilisant une cathode de platine. Ils ont trouvé qu'une solution contenant du chlorure de potassium 3 M et du chlorure stannique 0,3 M convenait pour le dosage du cérium (IV), de l'iode et du brome.

REFERENCES

[1] P. Arthur and J. E. Donahue, *Analyt. Chem.*, 1952, **24**, 1612.
[2] W. Oelsen and P. Gobbels, *Stahl u. Eisen*, 1949, **69**, 33.
[3] I. Sakai and S. Yuki, *Japan Analyst*, 1958, **7**, 33.
[4] W. D. Shults, P. F. Thomason and M. T. Kelley, *Analyt. Chem.*, 1955, **27**, 1750.
[5] D. J. Meier, R. J. Meyers and E. H. Swift, *J. Amer. Chem. Soc.*, 1949, **71**, 2340.
[6] A. J. Bard and J. J. Lingane, *Analyt. Chim. Acta*, 1959, **20**, 463.
[7] T. Takahashi, K. Kimoto and H. Sakurai, *Rep. Inst. Ind. Sci., Univ. of Tokyo*, 1955, **5**, 121.

Photometric titrations-IV:* The chelometric titration of cadmium in the presence of zinc

(*Received* 30 *May* 1961. *Accepted* 7 *June* 1961)

SWEETSER and BRICKER[1] described the EDTA titration of cadmium in the presence of zinc, with a photometric end-point at 236 mμ. The titration is performed in strongly alkaline medium where zinc is present as unreactive zincate, and cadmium is kept in solution by the addition of a small amount of cyanide. The disadvantages of this procedure are: operating at a very short wavelength, the high alkalinity, and the fact that the amount of cyanide added is critical. It therefore seemed worthwhile to search for a possibility of performing such a determination under more favourable conditions.

The numerical values of the stability constants of cadmium-chelonates are always very close to those of the corresponding zinc complexes with only one remarkable exception, namely, EGTA [ethyleneglycol-bis(aminoethyl)-tetra-acetic acid]. The logarithms of the stability constants of the EGTA complexes of cadmium and zinc are 16·7 and 12·8, respectively.[2] This difference of 3·9 logarithmic units refers to the absolute constants. In a practical titration the apparent stability constants have to be taken into account, and their difference can be increased by the use of an appropriate medium, such as an ammonia buffer. The logarithms of the β-factors of cadmium and zinc in an ammonia-ammonium chloride buffer pH 10 (total concentration 0·1*M*) are 3·9 and 8·6 respectively.[3] Hence the difference in the apparent stability constants under these conditions is 4·7 logarithmic units. This difference should be sufficient to permit the potentiometric titration of

* Part III—see *Talanta*, 1961, **8**, 885.

the coulometric titration of cerium^{IV} ion and iodine used the potentiometric method and that of bromine used the amperometric method. In the amperometric detection, the indicating current was expressed with the voltage drop measured through the definite resistance, when the voltage 0·3 ~ 0·4 V was applied between the two platinum electrodes through 100 kΩ resistance.

In conclusion, the coulometric method with tin^{II} ion is considered to be more versatile using a solid electrode such as platinum than that with titanium^{III} or chromium^{II} ions in which cases the mercury electrode is forced to be employed in place of the solid electrode.

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Summary—The coulometric method of electrogenerated tin^{II} ion using the platinum electrode as a generating cathode has been investigated. The electrolytic solution comprising 3*M* potassium chloride and 0·3*M* tin^{IV} chloride has been found to be satisfactory for the determination of cerium^{IV} ion, iodine and bromine with an error of only a few percent provided suitable conditions are employed.

Zusammenfassung—Coulometrie mit Zinn(II)-ionen (an einer Platinelektrode erzeugt) wurde untersucht. Eine elektrolyt welcher 3M in Kaliumchlorid und 0,3M in Stannichlorid ist wurde für die Titration von Cer(IV), Jod und Brom geeignet gefunden.

Résumé—Les auteurs ont étudié la coulométrie à l'aide de l'ion stanneux préparé par électrolyse, en utilisant une cathode de platine. Ils ont trouvé qu'une solution contenant du chlorure de potassium 3 M et du chlorure stannique 0,3 M convenait pour le dosage du cérium (IV), de l'iode et du brome.

REFERENCES

[1] P. Arthur and J. E. Donahue, *Analyt. Chem.*, 1952, **24**, 1612.
[2] W. Oelsen and P. Gobbels, *Stahl u. Eisen*, 1949, **69**, 33.
[3] I. Sakai and S. Yuki, *Japan Analyst*, 1958, **7**, 33.
[4] W. D. Shults, P. F. Thomason and M. T. Kelley, *Analyt. Chem.*, 1955, **27**, 1750.
[5] D. J. Meier, R. J. Meyers and E. H. Swift, *J. Amer. Chem. Soc.*, 1949, **71**, 2340.
[6] A. J. Bard and J. J. Lingane, *Analyt. Chim. Acta*, 1959, **20**, 463.
[7] T. Takahashi, K. Kimoto and H. Sakurai, *Rep. Inst. Ind. Sci., Univ. of Tokyo*, 1955, **5**, 121.

Photometric titrations-IV:* The chelometric titration of cadmium in the presence of zinc

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SWEETSER and BRICKER[1] described the EDTA titration of cadmium in the presence of zinc, with a photometric end-point at 236 mμ. The titration is performed in strongly alkaline medium where zinc is present as unreactive zincate, and cadmium is kept in solution by the addition of a small amount of cyanide. The disadvantages of this procedure are: operating at a very short wavelength, the high alkalinity, and the fact that the amount of cyanide added is critical. It therefore seemed worthwhile to search for a possibility of performing such a determination under more favourable conditions.

The numerical values of the stability constants of cadmium-chelonates are always very close to those of the corresponding zinc complexes with only one remarkable exception, namely, EGTA [ethyleneglycol-bis(aminoethyl)-tetra-acetic acid]. The logarithms of the stability constants of the EGTA complexes of cadmium and zinc are 16·7 and 12·8, respectively.[2] This difference of 3·9 logarithmic units refers to the absolute constants. In a practical titration the apparent stability constants have to be taken into account, and their difference can be increased by the use of an appropriate medium, such as an ammonia buffer. The logarithms of the β-factors of cadmium and zinc in an ammonia-ammonium chloride buffer pH 10 (total concentration 0·1*M*) are 3·9 and 8·6 respectively.[3] Hence the difference in the apparent stability constants under these conditions is 4·7 logarithmic units. This difference should be sufficient to permit the potentiometric titration of

* Part III—see *Talanta*, 1961, **8**, 885.

cadmium in the presence of zinc employing the mercury drop electrode.[4] This approach is at present under investigation in the authors' laboratory.

The difference of barely five logarithmic units represents a border-line case for a visual titration when a complex-forming indicator is employed. In addition to this, there is no indicator known which reacts specifically with cadmium, and the hope of ever finding one seems to be very slight.

The difference of 4·7 log-units is more than sufficient for a photometric end-point, provided that either of the two metal-systems is self-indicating.[5] This, however, is not the case, since all species involved are colourless. A possibility may exist in the ultraviolet region, but this has not been investigated. Theoretical considerations indicate the possibility of placing a self-indicating system having an appropriate stability constant between that of the cadmium and zinc. For example, Underwood used copper as photometric indicator in the EDTA titration of bismuth.[6] Copper is especially suitable for this purpose because of the relatively large difference of the extinction coefficients of the free copper ion or its amino complex and any chelon complex. The stability constant of the copper-EGTA complex has not yet been reported in the literature. It is, however, reasonable to assume that it will be of the same order as, or even somewhat greater than, that of the cadmium complex. Fortunately the logarithm of the β-factor for copper in an ammonia buffer as specified above is 8·3.[3] This makes it possible to arrange the apparent stability constants in the order Cd $>$ Cu $>$ Zn. Experiments verified this assumption. Thus, a titration of cadmium in the presence of zinc is possible with copper as the photometric indicator.

EXPERIMENTAL

Apparatus

The photometric titrator used was described in an earlier paper in this series.[7] Cuvettes with a light path of 3 and 10 cm and a capacity of about 100–200 ml were employed. A Sargent automatic burette was used.

Reagents

Solutions of metals ions and complexing reagent were prepared from Reagent Grade material and standardised according to well-established chelometric procedures.[8,9] The buffer, pH 10, was prepared by dissolving 70 g of ammonium chloride and 570 ml of conc. ammonia in de-ionised water and diluting to 1 litre.

Absorbance curves of copper in solutions containing buffer (pH 10) in the absence of EGTA and in the presence of excess EGTA show that the most suitable wavelength for the titration is between 700 and 750 mμ. A 742-mμ interference filter was used.

Procedure

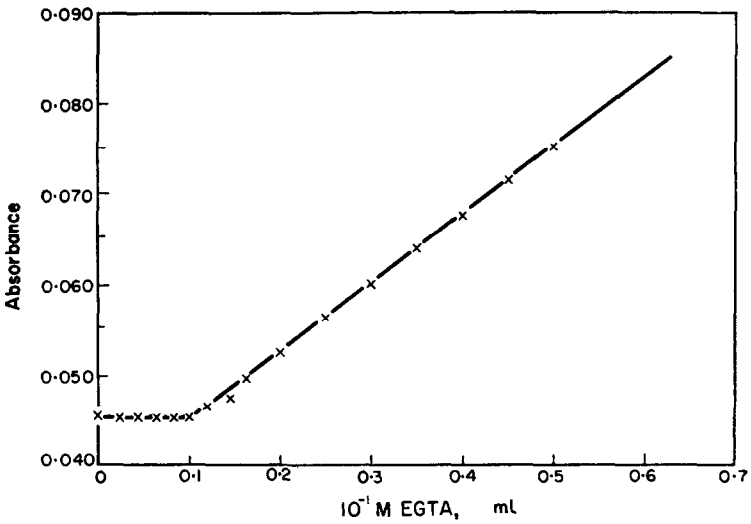
Accurately measured amounts of cadmium and zinc solutions were pipetted into the titration cell, 10 ml of buffer, pH 10 (the amount of buffer is not critical), and 5 ml of 0·1*M* solution of copper sulphate were added, and diluted to about 150 ml with de-ionised water. The cell was placed in the phototitrator, and the titration was performed in the usual manner. The transmittance readings were plotted on semi-log paper or, in the case of small changes, more conveniently transformed to absorbance and plotted on linear paper.

RESULTS

A representative curve is shown in Fig. 1. The results of some titrations are presented in Table I.

When the concentration of zinc is not exceedingly high the titration can be extended to a second, but less sharp, end-point thus permitting the determination of cadmium *and* copper in the presence of zinc.

Iron and aluminium in moderate amounts, when masked with tartrate, do not interfere. Magnesium can be present in considerable quantities. Most of the other ions interfere as in other chelometric procedures; they are either co-titrated, *e.g.*, lead and calcium, or cause a decrease in the slope difference, *e.g.*, nickel. This, however, is no serious drawback, since the separation of cadmium and zinc from most other elements can readily be effected by ion-exchange methods.[10] On the other hand, some multicomponent systems can be resolved by chelometric titrations involving operation with aliquots and employing different masking reagents, titrants and indicators. Where up till now the sum of cadmium plus zinc has been determined, the cadmium may be determined in a further step incorporating the new method.



0.1*M* Zn (total volume about 150 ml; cell length 10 cm; 742 mμ).

FIG. 1.—Titration curve for the determination of 2·00 ml of 5 × $10^{-3}M$ Cd in the presence of 50 ml of 0·1*M* Zn (total volume about 150 ml; cell length 10 cm; 742 mμ).

TABLE I. TITRATION OF CADMIUM WITH 0·1*M* EGTA IN THE PRESENCE OF ZINC, 742 mμ

Cd			Zn, *ml*		Cd:Zn *Ratio*
Taken, *ml*	Found, *ml*				
4·00	4·00	0·1*M* 3-cm cell	0		—
9·90	9·94		25		1:25
4·00	4·02		5		1:1·25
4·00	3·95		100		1:25
2·03	2·06	$5 \times 10^{-3}M$ 10-cm cell	0	0·1*M*	—
10·00	10·00		25		1:50
2·03	2·00		10		1:100
3·56	3·64		50		1:260
1·01	1·04		15		1:300
2·03	2·08		50	0·2*M*	1:500

The following example may show the principle of this approach. The sample contained the following ions: Pb, Zn, Cd and Cu.

In the first aliquot Pb was titrated with EDTA (Eriochrome Black T as indicator) in the presence of tartrate and cyanide. After selective demasking of Zn and Cd with formaldehyde, the titration was continued to obtain the sum Zn + Cd. In a second aliquot the sum Pb + Cd was obtained employing the new method. In a third aliquot the sum of all metals present was obtained by an EDTA titration at pH 6 using PAN as indicator.

The following results were obtained; the first figure is the calculated value, the second figure the experimental one.

Pb: 3·82; 3·80. Cd: 1·05; 1·08. Zn: 5·45; 5·40. Cu: 2·18; 2·26.

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Summary—A new method for the photometric titration of cadmium in the presence of zinc using ethyleneglycol-bis(aminoethyl)-tetra-acetic acid is described. Copper ion in ammonical solution serves as photometric indicator. One ml of 0·01 Cd solution in a total volume of about 150 ml was determined in the presence of a 500-fold excess of zinc.

Zusammenfassung—Eine neue Methode zur photometrischen Titration von Cadmium neben Zink mit Äthylenglocol-bis(aminoäthyl) tetressigsäure wird beschrieben. Kupferion in ammoniakalischer Lösung dient als photometrischer Indicator. 1 ml 0·01 m Cd-Lösung in 150 ml Titrationsvolum konnte neben der 500 fachen Menge Zink bestimmt werden.

Résumé—Les auteurs décrivent une nouvelle méthode de dosage photométrique du cadmium, en présence de zinc, par l'acide éthylène-glycol-bis(aminoéthyl) tétracétique. L'ion cuivre en solution ammoniacale sert d'indicateur photométrique. Un ml de solution de cadmium 0,01 M dans un volume total d'environ 150 ml a été dosé en présence d'un excès de zinc 500 fois plus important.

REFERENCES

[1] P. S. Sweetser and C. E. Bricker, *Analyt. Chem.*, 1954, **26**, 195.
[2] A. Ringbom, G. Pensar and E. Wänninen, *Analyt. Chim. Acta*, 1958, **19**, 525.
[3] E. Wänninen, *Acta Acad. Abonensis*, 1960, **21**, 104.
[4] C. N. Reilley and R. Schmid, *Analyt. Chem.*, 1958, **30**, 947.
[5] H. Flaschka, *Talanta*, 1961, **8**, 381.
[6] A. L. Underwood, *Analyt. Chem.*, 1954, **26**, 1322.
[7] H. Flaschka and P. O. Sawyer, *Talanta*, 1961, **8**, 521.
[8] G. Schwarzenbach, *Die komplexometrische Titration*. F. Encke, Stuttgart, 1956.
[9] H. Flaschka, *EDTA Titrations*, Pergamon Press, London, 1959.
[10] K. H. Kraus and G. E. Moore, *J. Amer. Chem. Soc.*, 1953, **75**, 1960.

Semimicro determination of strontium and calcium in mixtures*

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INTRODUCTION

THE determination of strontium and calcium in a mixture is one of the most difficult and troublesome problems in analytical chemistry, because of the similarity of their properties. The gravimetric procedures described are not free from co-precipitation and therefore if a quantitative determination is needed, several precipitations must be effected. The commonly used procedure is by precipitating strontium nitrate in a mixture of alcohol-ether[1] thus separating it from calcium, followed by the gravimetric determination of the strontium as sulphate, or oxide, and the determination of calcium as oxide, or titrimetrically. Weiss and Shipman[2] used potassium rhodizonate in a gravimetric method for the separation of strontium-90 from calcium. According to their paper, about 80 to 90% strontium can be recovered when the ratio Ca:Sr is as high as 50, using a four-fold excess of rhodizonate. Lieser and Hild[3] determined the solubility of strontium rhodizonate in solution. Their results show that under appropriate conditions the separation between calcium and strontium can be effected quantitatively by this reagent. In the present study we attempted to find suitable conditions for (*a*) a quantitative separation of strontium and calcium by rhodizonate; (*b*) a rapid determination of both ions, without using radiochemical techniques.

Calcium and strontium were determined by a complexometric method.[4] To permit this the rhodizonate had to be eliminated, because its presence interfered in the titrations. The conditions for this elimination were also studied.

* This investigation was initiated and sponsored by the Israel Atomic Energy Commission, and is published with their permission. A full version of this paper is published as a report in the Israel Atomic Energy Bulletin, No. 695 1961.

Summary—A new method for the photometric titration of cadmium in the presence of zinc using ethyleneglycol-bis(aminoethyl)-tetra-acetic acid is described. Copper ion in ammonical solution serves as photometric indicator. One ml of 0·01 Cd solution in a total volume of about 150 ml was determined in the presence of a 500-fold excess of zinc.

Zusammenfassung—Eine neue Methode zur photometrischen Titration von Cadmium neben Zink mit Äthylenglocol-bis(aminoäthyl) tetressigsäure wird beschrieben. Kupferion in ammoniakalischer Lösung dient als photometrischer Indicator. 1 ml 0·01 m Cd-Lösung in 150 ml Titrationsvolum konnte neben der 500 fachen Menge Zink bestimmt werden.

Résumé—Les auteurs décrivent une nouvelle méthode de dosage photométrique du cadmium, en présence de zinc, par l'acide éthylène-glycol-bis(aminoéthyl) tétracétique. L'ion cuivre en solution ammoniacale sert d'indicateur photométrique. Un ml de solution de cadmium 0,01 M dans un volume total d'environ 150 ml a été dosé en présence d'un excès de zinc 500 fois plus important.

REFERENCES

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[3] E. Wänninen, *Acta Acad. Abonensis*, 1960, **21**, 104.
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Calcium and strontium were determined by a complexometric method.[4] To permit this the rhodizonate had to be eliminated, because its presence interfered in the titrations. The conditions for this elimination were also studied.

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EXPERIMENTAL

Reagents

The reagents used were all of analytical grade. The aqueous rhodizonate solution (0·2%) was always freshly prepared from the sodium rhodizonate salt (B.D.H.). The EDTA solution was standardised by titration against a standard solution of strontium or calcium nitrate. The complexometric indicator, which was not stable for more than 2–3 days, was prepared by dissolving 0·1 g of *o*-cresolphthaleincomplexone (B.D.H.), 0·05 g of methyl red and 0·05 g of bromocresol green in a few drops of concentrated ammonia and diluting to 100 ml with water.[5]

Procedure

(*a*) *Separation of strontium and calcium:* The pH of the solutions with appropriate contents of calcium and strontium is adjusted to a value between 6–7. If the solutions to be analysed are acid, neutralisation can only be effected by potassium hydroxide. The volume of the solution should be about 15 ml. A two-fold excess of rhodizonate to strontium is added, with continuous stirring. After 5 min standing, the precipitate is filtered through Whatman No. 42 filter paper. The precipitate is washed on the filter with small amounts of water (10–15 ml) and dissolved in 15 ml of 0·5*N* HNO_3. This solution is used for the determination of strontium after the elimination of the rhodizonate. The rhodizonate must also be removed from the filtrate for the determination of calcium.

(*b*) *Elimination of rhodizonate:* The acid solution of strontium and rhodizonate is neutralised with a few drops of 1*N* NaOH until a brown-reddish colour appears. The solution is passed through a column, 16 mm in diameter and 180 mm long, filled to 3/4 of its length with the anion-exchange resin Amberlite IRA 410 Cl-technical, and the resin is then washed with 50 ml of water, the washings being added to the eluate. The solution of calcium is passed through the same column without neutralisation.

To save time, the precipitate of strontium rhodizonate is filtered through a filter funnel which is placed directly above the ion-exchange column. By this procedure, the filtrate containing the calcium has the rhodizonate removed immediately.

(*c*) *Complexometric titrations:* (*i*) *Titration of calcium:* 15–20 ml of saturated NH_4Cl, 5 ml of conc. NH_4OH, 10–15 ml of alcohol and 5–6 drops of the indicator are added to the solution. The solution is titrated with 0·02*N* EDTA until the red colour disappears abruptly. (*ii*) *Titration of strontium:* 5 ml of conc. NH_4OH, 40–50 ml of alcohol and 5–6 drops of the indicator are added to the solution. The titration is carried out with 0·05*N* EDTA, to the same end-point.

RESULTS AND DISCUSSION

The conditions for the quantitative precipitation of strontium rhodizonate without the co-precipitation of calcium were studied. As the presence of sodium and ammonium ions interfere with the precipitation by rhodizonate, acid solutions can only be brought to the required pH by neutralisation with potassium hydroxide. As can be seen from the results (Table I) the greatest accuracy was obtained with mixtures containing about 5 mg of strontium and 0–5 mg of calcium in about 10–15 ml solution. Only a twofold excess of rhodizonate to the strontium was needed, and the precipitate obtained could be filtered after a few min. Under these conditions the co-precipitation of calcium was avoided.

The rhodizonate could be eliminated in two different ways:

(a) heating to dryness,

(b) ion exchange.

The first procedure prolonged the time needed for the determination by 3–12 hr, and therefore, the ion-exchange method was used. It was found that by using a small column, filled with anion-exchanger in the chloride form, the rhodizonate from the solutions was removed in about 15 min. The optimum pH for the exchange was found to be 6, and acid solutions of strontium rhodizonate were adjusted to this pH with a sodium hydroxide solution. It was also found that the removal of rhodizonate occurred more easily when the precipitate was dissolved in nitric acid than in hydrochloric acid.

The solutions containing calcium and strontium were titrated with EDTA after the addition of alcohol, ammonia, ammonium chloride and *o*-cresolphthaleincomplexone. The quantity of alcohol added influenced the end-point in the case of strontium. It was found that 40–50 ml of alcohol

TABLE I.—ANALYSIS OF MIXTURES OF CALCIUM AND STRONTIUM

Taken, *mg*		Found, *mg*		Deviation, *mg*		Deviation, %		No. of determns.
Sr	Ca	Sr	Ca	Sr	Ca	Sr	Ca	
4·99	—	5·00	—	+0·01	—	0·2	—	4
—	5·02	—	5·10	—	−0·08	—	1·5	4
4·99	2·51	5·00	2·53	+0·01	+0·02	0·2	0·8	6
5·00	5·02	5·10	4·88	+0·10	−0·14	2·0	2·8	4
9·99	5·15	10·98	4·70	+0·99	−0·45	10·0	8·0	4
4·99	~0·6	5·04	0·56	+0·05		1·0		4

were necessary for reproducible results. Titration effected with 0·01*N* EDTA showed no clear end-points. It was found that for calcium 0·02–0·1*N* EDTA could be used, while for strontium the smallest usable normality was 0·05. Complexometric titrations with other indicators were attempted but the best results were obtained by the *o*-cresolphthaleincomplexone mixture described above although the end-point was not very sharp.

Summary—A method is described for the quantitative separation and determination of about 5 mg of strontium and 0·5–5 mg of calcium, by precipitation of strontium at pH ~ 6 with sodium rhodizonate, and determination of both ions by complexometric titrations.

Zusammenfassung—Eine Methode zur quantitativen Trennung und Bestimmung von etwa 5 mg Strontium und 0·5–5 mg Calcium durch Fällung von Strontium mit Natrium-Rhodizonat bei pH ~6 und komplexometrische Titrierung der beiden Ionen wird beschrieben.

Résumé—Les auteurs décrivent une méthode de séparation et de dosage d'environ 5 mg strontium et de 0,5–5 mg calcium par précipitation du strontium par le rhodizonate de sodium à pH ~6 et dosage des deux ions par titrages complexométriques.

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REFERENCES

[1] W. W. Scott, *Standard Methods of Chemical Analysis.* D. Van Nostrand Company, Inc., Vol. I, p. 123.
[2] H. V. Weiss and W. H. Shipman, *Analyt. Chem.*, 1957, **29**, 1764.
[3] K. H. Lieser and W. Hild, *Z. Naturforsch.*, 1960, **15b**, 62.
[4] G. Anderegg, H. Flaschka, R. Sallmann and G. Schwarzenbach, *Helv. Chim. Acta*, 1954, **37**, 113.
[5] Frank J. Welcher, *The Analytical Uses of Ethylenediaminetetra-acetic acid.* D. Van Nostrand Co., 1958, pp. 106, 115, 143.

A spot test for uranium^{VI} with resacetophenone-oxime

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RESACETOPHENONE-OXIME was recommended by Neelakantam and co-workers[1,2] for the colorimetric determination of iron^{III} and uranium^{VI}. A reddish-brown colour was developed on the addition of the reagent to uranium^{VI} in a weak mineral acid medium. The intensity of the colour was found to increase with an increase in pH of the solution. This paper presents the results of the experiments carried out to establish the limit of identification of uranium^{VI} using resacetophenone-oxime.

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5·00	5·02	5·10	4·88	+0·10	−0·14	2·0	2·8	4
9·99	5·15	10·98	4·70	+0·99	−0·45	10·0	8·0	4
4·99	~0·6	5·04	0·56	+0·05		1·0		4

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REFERENCES

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[4] G. Anderegg, H. Flaschka, R. Sallmann and G. Schwarzenbach, *Helv. Chim. Acta*, 1954, **37**, 113.
[5] Frank J. Welcher, *The Analytical Uses of Ethylenediaminetetra-acetic acid.* D. Van Nostrand Co., 1958, pp. 106, 115, 143.

A spot test for uranium^{VI} with resacetophenone-oxime

(*Received* 6 *June* 1961. *Accepted* 17 *July* 1961)

RESACETOPHENONE-OXIME was recommended by Neelakantam and co-workers[1,2] for the colorimetric determination of iron^{III} and uranium^{VI}. A reddish-brown colour was developed on the addition of the reagent to uranium^{VI} in a weak mineral acid medium. The intensity of the colour was found to increase with an increase in pH of the solution. This paper presents the results of the experiments carried out to establish the limit of identification of uranium^{VI} using resacetophenone-oxime.

EXPERIMENTAL

Reagents

Uranium^{VI} nitrate: AnalaR uranium^{VI} nitrate was dissolved in water. This solution was standardised by gravimetric[3] and titrimetric[4] methods. It was suitably diluted for spot-test analysis.

Resacetophenone-oxime: A 0·5% solution of this reagent in alcohol.

Procedure for the spot test

0·05 Ml of the uranium^{VI} nitrate solution was taken on a spot plate and 0·05 ml of the reagent solution was added to this and the two were thoroughly mixed. The observations were made after 30 sec. It was found that the red-brown colour of the uranium^{VI}–resacetophenone-oxime complex could be perceived with $5{\cdot}0 \times 10^{-5}$ *M* uranium^{VI} solution. With lower concentrations of uranium^{VI}, no colour could be observed.

Effect of pH

The effect of pH was studied using $5{\cdot}5 \times 10^{-5}$ *M* uranium^{VI} solution. It was noticed that lowering of the pH below 5·6 adversely affected the colour development whereas increase in pH by the addition of ammonia enhanced the intensity of the colour appreciably. When 0·05 ml of uranium^{VI}, 0·05 ml of the reagent solutions and 0·1 ml of 1*N*–11*N* ammonia were mixed, it was found that the brown colour could be observed using even $1{\cdot}25 \times 10^{-5}$ *M* uranium^{VI} solution.

Limit of identification = 0·595 μg
Dilution limit = 1:3,400,000

Interferences

Over a wide range of pH the reagent did not give any colour with uranium^{IV} even on keeping for long periods. Aluminium, zirconium and thorium did not interfere with the test. Iron^{III} was found to give a deep purple colour with the reagent and this reaction enables one to detect 1·2 μg of iron^{III}.

Application to titrations

Resacetophenone-oxime can be used as an external indicator in the titration of orthophosphate solution with uranium^{VI}. Interferences are the same as when conventional indicators are used. The recommended procedure is as follows:

A known volume of standard potassium dihydrogen phosphate solution is taken in a beaker, and 5 ml of acetic acid–sodium acetate buffer solution (pH, during titration, could be varied between 3·6 and 5·6) per 50 ml of titration mixture are added. The mixture is heated to 80° and titrated with uranium^{VI} solution. The end-point, which is very distinct, is indicated by the appearance of a reddish-brown colour when one drop of the titration mixture is mixed thoroughly with two drops of the resacetophenone-oxime solution and two drops of ammonia on a spot plate.

Acknowledgment—The author is grateful to Professor K. Neelakantam for his keen interest and guidance in this work.

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Summary—A spot test for the detection of uranium^{VI} using resacetophenone-oxime is developed. It is found that a reddish brown colour develops when solutions of uranium^{VI} and resacetophenone-oxime are mixed in ammoniacal medium. The limit of identification is 0·595 μg.

Zusammenfassung—Ein Tüpfelnachweis für Uran(VI) mit Resacetophenonoxim wird beschrieben. Eine rötlichbraune Färbung entsteht in ammoniakalischem Medium. Die Nachweisgrenze beträgt 0·595 μg.

Résumé—L'auteur met au point un essai par touches pour déceler l'uranium(VI) en utilisant le resacétophénone-oxime. Une couleur brun rougeâtre se forme quand des solutions d'uranium (VI) et

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de resacétophénone-oxime sont mélangées en milieu ammoniacal. La limite d'identification trouvée est de 0.595 μg.

REFERENCES

[1] K. Neelakantam and M. V. Sitaraman, *Curr. Sci.*, 1945, **14**, 320.
[2] K. Neelakantam and M. Kantharajurs, *J. Sci. Ind. Res.*, 1952, **11B**, 78.
[3] Frank J. Welcher, *Organic Analytical Reagents.* D. Van Nostrand Company Inc., New York, Vol. III, 1955, p. 384.
[4] C. E. F. Lundell and H. B. Knowles, *J. Amer. Chem. Soc.*, 1925, **47**, 2637.

A qualitative test for detection of ferrocenes

(*Received* 10 *July* 1961. *Accepted* 21 *August* 1961)

THE value of a diagnostic test for the detection of the ferrocene nucleus in reaction mixtures resulting from attempted "sandwiching" reactions to prepare ferrocene derivatives has been pointed out by Goldberg[1] in his report of such a test. A similar test method has also been applied to the separation and detection of ferrocenes.[2] We now wish to report an alternative test based on an original observation which is believed to provide a simpler procedure.

The previous method[1] involved separating the ferrocene constituent in the sample which was suspected of containing a ferrocene derivative from the materials in the reaction mixture on a paper chromatogram, treating the chromatogram with hydrogen peroxide to destroy the ferrocene nucleus and to oxidise the iron^{II} to iron^{III} and then detecting the iron^{III} as a red thiocyanate complex.* The method now being reported is based on the observation that various ferrocene derivatives, when dissolved in glacial acetic acid and treated directly with aqueous potassium cyanoferrate^{III}, gave an immediate colour change somewhat similar to that obtained with iron^{II} ion.

The present test method involves simply extracting, with chloroform, a small sample of a reaction mixture previously made aqueous, placing 2 drops of the chloroform extract in approximately 3 ml of glacial acetic acid, and treating with 2 drops of aqueous potassium cyanoferrate^{III} (approximately 1 g/10 ml). In dilute solutions the presence of a ferrocene derivative is indicated by the appearance of a clear green colour, whereas in more concentrated solutions a deep blue precipitate separates.

Results obtained in applying the cyanoferrate^{III} test to a number of different ferrocene derivatives are shown in Table 1. Although colour changes were obtained with all of these derivatives some minor deviations from the general behaviour noted above were observed. The difference in colour observed with 1,1'-dibenzoylferrocene may result from the original deep red colour of the solution of this compound, which undoubtedly masks the true colour change. The mono- and diethyl-esters of ferrocene dicarboxylic acid gave unusually weak responses to this test compared with the other derivatives. Although the quantitative sensitivity of this test was not established, a positive test was obtained with the parent compound, ferrocene, using as little as 1 drop of solution containing 0·1 g of ferrocene in 100 ml of chloroform.

This test is believed to have advantages over the previously described methods for detection of the ferrocene nucleus in that it is simpler and more rapid. It requires no chromatogram or separate step to oxidise and destroy the ferrocene nucleus, and it provides an immediate answer with only a few drops of test solution. The test can be carried out in a test tube or on a spot-test plate. The chloroform extraction required for the test can be part of the normal working up of the reaction mixture, or it may be carried out on a small sample withdrawn from the reaction mixture by shaking with an aqueous-chloroform mixture in a test tube. The nature of the chemical change which occurs in the cyanoferrate^{III} test is at present under investigation; the results of this study will be reported upon at a later date.

* It is apparently not necessary to destroy completely the ferrocene nucleus since it has recently been reported[3] that the ferricinium ion also provides a colored complex with thiocyanate.

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TABLE I. FERROCENES (4,5) TESTED WITH $K_3Fe(CN)_6$*

Compound tested	Observed change	
	Dil. soln.	Conc. soln.
Ferrocene	Green colour	Blue ppt.
Benzoylferrocene	Green colour	Blue ppt.
1,1′-Dibenzoylferrocene	Yellow-green colour	Green-brown ppt.
2-Hydroxybenzoylferrocene	Blue ppt.	Blue ppt.
2-Methoxybenzoylferrocene	Green colour	Blue ppt.
2,4-Dihydroxybenzoylferrocene	Green colour	Blue ppt.
2-Hydroxy-4-methoxybenzoylferrocene	Green colour	Blue ppt.
2,4-Dimethoxybenzoylferrocene	Green colour	Blue ppt.
Ferrocenemonocarboxylic acid	Green colour	Blue ppt.
Ethyl ferrocenemonocarboxylate	Green colour	Blue ppt.
1-Carboxy-1′-carbethoxyferrocene	V. lt. green colour	Lt. green colour
1,1′-Diethyl ferrocenedicarboxylate	V. lt. green colour	Lt. green colour
1,1′-Bis(α-hydroxyethyl)-ferrocene	Green colour	Blue ppt.
Diferrocenyl ketone	Green colour	Blue ppt.
1,1′-Bis(chloromethyldimethylsilyl)ferrocene	Green colour	Blue ppt.

* To determine whether $iron^{II}$, which is employed in the "sandwiching" reactions, or $iron^{III}$ which might be present, could interfere with this test, both aqueous and aqueous-tetrahydrofuran solutions of $iron^{II}$ and $iron^{III}$ chlorides were extracted with chloroform and the extracts were subjected to the test. None of these extracts provided a positive test.

Acknowledgements—With the exception of the parent compound, ferrocene, which was a recrystallised sample of material purchased from Ethyl Corporation, all of the ferrocene derivatives listed in Table I were analytically pure samples prepared and purified by Robert L. Schaaf[4,5] under contract with Materials Central, Wright Air Development Division.

Summary—The detection of the ferrocene nucleus of various substituted ferrocenes by a colour reaction with cyanoferrate^{III} ion is reported.

Zusammenfassung—Ein neuer Test wird mitgeteilt um Nachweis von Ferrozinkerne hingewiesen.

Résumé—L'auteur décrit un essai pour la detéction des ferrocènes.

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REFERENCES

[1] S. I. Goldberg, *Analyt. Chem.*, 1959, **31**, 486.
[2] A. N. Belder, E. J. Bourne and J. B. Pridham, *Chem. and Ind.*, 1959, 996.
[3] T. D. Smith, *J. Chem. Soc.*, 1961, 473.
[4] R. L. Schaaf, *J. Org. Chem.*, submitted.
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A phosphorus pentoxide desiccant employing exfoliated vermiculite as carrier

(*Received* 6 *October* 1961. *Accepted* 20 *October* 1961)

INTRODUCTION

PHOSPHORUS pentoxide has been consistently employed as a desiccant for dehydration of air and other gases. It has been popularly considered to be as near perfect in drying efficiency as any form of solid material.

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INTRODUCTION

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Unfortunately, it exhibits many objectionable properties. It is a powder, acid in reaction and low in drying capacity; and it is extremely difficult to handle, except by employing dry-box manipulative techniques. In "drying pistols" for desiccation of chemicals at controlled temperatures, surface incrustations of spent desiccant soon form. The reagent reservoir is thus prematurely and effectively inactivated.

An inert carrier-base, exfoliated vermiculite of high porosity, has been found to correct most of these faults.

EXFOLIATED VERMICULITE AS CARRIER

Exfoliated vermiculite has been previously described[1] for use as a carrier-base absorbent for the preparation of granular anhydrous magnesium perchlorate as desiccant. Sifted samples were prepared. Mesh sizes passing 8 and retained by 12, and passing 12 and retained by 20, were employed. The bulk density was found to be 0·17 and 0·21 g per ml, respectively. Exfoliated vermiculite is a common product of the building trades. It is employed as a free-flowing thermal insulator, and costs only a few pence per pound.

PREPARATION OF CARRIER-BASED DESICCANT

A weighed amount of carrier is placed in a dry 1000-ml screw-top bottle. An equal weight of P_2O_5 is quickly added and the bottle is closed. The bottle and contents (only half full) are then shaken vigorously for 5 min. The powdered P_2O_5 is thus incorporated completely within the voids of the exfoliated carrier. The bulk density of the finished product is thereby doubled. The finished product is a dust-free and free-flowing granular product.

DESICCANT CAPACITY OF CARRIER-BASED PHOSPHORUS PENTOXIDE

An absorption tube (25 × 350 mm) charged with 8–12 mesh granules, contained 28·2 g of desiccant. When saturated with water from a continuous flow of air of high humidity, its capacity was found to be 5·15 g of water or 18·3 % of its original weight. The spent reagent is free flowing and alters in colour from grey to that of the untreated carrier base, a colour transition which is readily observed.

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Iowa State University, Ames, U.S.A. Harvey Diehl

Summary—A granular carrier based phosphorus pentoxide of selective mesh sieve size aggregates is described. The water absorption capacity at maximum efficiency is 18·3 percent of reagent weight. This desiccant, as compounded, and as the spent material, is simple to prepare from commercially available materials and free flowing.

Zusammenfassung—Phosphorpentoxyd als Trockenmittel auf einem Träger und in bestimmter Korngrösse wird beschrieben. Die Absorptionskapazität in Bezug auf Wasser beträgt maximal 18·3 % des Reagensgewichtes. Das vor und nach Absorption frei schüttbare Granulat ist leicht aus käuflich erhältlichen Materialien herstellbar.

Résumé—Les auteurs décrivent un support granulaire à base de pentoxyde de phosphore, en agrégats de dimension sélectionnée. La capacité d'absorption de l'eau, pour une efficacité maximum, est de 18,3 pour cent du poids du réactif. Ce desséchant est simple à préparer à partir de produits disponibles dans le commerce.

REFERENCE

[1] G. Frederick Smith and Harvey Diehl. *Talanta*, in the press.

Talanta, 1962, Vol. 9, pp. 86 to 88. Pergamon Press Ltd. Printed in Northern Ireland

LETTERS TO THE EDITOR

The determination of tantalum, niobium and titanium by precipitation from homogeneous solution

Sir,

As was already shown in a previous article,[1] tungsten can be successfully determined by precipitation from a homogeneous hydrogen peroxide-nitric acid solution. The same procedure is readily adaptable to the determination of niobium and tantalum. After a potassium bisulphate fusion, the melt is dissolved in hydrogen peroxide and nitric acid, and subjected to thermal decomposition of the soluble peroxides. Tracer techniques showed that the recovery is better than 99.8%, whereas the co-precipitation of titanium is negligible.

Precipitation from homogeneous solution of niobium, tantalum and titanium is also possible by thermal decomposition of their peroxides from a slightly alkaline medium (pH = 7–8), with low tungsten co-precipitation.

By alternative precipitation from homogeneous solution in a nitric acid and an alkaline medium, it thus becomes possible to determine the tungsten, niobium + tantalum and titanium contents of a sample after a titanium and tungsten determination in the respective filtrates.

The co-precipitation distribution constants of titanium and tungsten for both procedures were determined. They appeared to follow Riehl's law.

A full account of this work will be published in due course.

Laboratory for Analytical Chemistry
Ghent University, Belgium
22 *August* 1961

R. DAMS
J. HOSTE

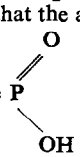
REFERENCES

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Infrared spectra of some organophosphorus extractants

SIR,

The recent paper by Horton and White[1] contains errors in the assignment of absorption bands which should be corrected to prevent their perpetuation by future workers. The authors do not appear to have realised the danger of the application of published correlations without due regard to the chemistry and constitution of the compounds being examined. Typical examples are the assignment of a band in the spectrum of capryl phenylphosphonic acid[2] to a P-O-(aryl) vibration, when the molecule contains a P-aryl rather than a P-O-(aryl) bond, and the comment on the strength of the P-H absorption band in trialkyl phosphites,[3] which contain no P-H bonds.

The attribution throughout the paper of absorption in the region of 2400 cm^{-1} to P-H impurities, is also open to criticism. Absorption due to the P-H valence vibration undoubtedly occurs in this region but the P-H bands are sharp, are of medium intensity, and are invariably accompanied by a sharp, medium to strong, band, in the region of 1100 cm^{-1}, which is assigned[4] to the P-H deformation vibration. Inspection of the published spectra strongly suggests that the absorption near 2400 cm^{-1} is caused by the second of the three bands, characteristic of the  group[5,6] arising from the presence of an acidic impurity.

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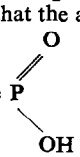
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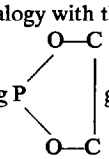
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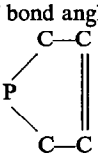
Similarly, the absorption bands reported[7] in the region 3300–3700 cm^{-1} may have a common source. Experience has shown that it is difficult to prepare organo-phosphorus compounds completely free of water and to exclude all water during subsequent storage and the handling stages preparatory to running a spectrum. The reported bands are probably caused by a trace of adsorbed water. The exact position of the band will vary both with the concentration of the water in the phosphorus compound and with the dilution of the latter in the solvent. The band detected at 3500 cm^{-1} in dibutyl hydrogenphosphonate is certainly not due to hydrogen bonded hydroxyl connected with the postulated dimeric structure, since this contains no hydroxyl groups. Also the observed phosphoryl frequency is somewhat higher than the calculated value, indicating that the P—O bond is not involved in hydrogen bonding. Furthermore, it has been shown by Fox,[8] as quoted by Doak and Freedman,[9] that the concentration of the phosphite isomer in dibutyl hydrogenphosphonate is about 10^{-4}%. At this level it is not surprising that the (P)—O—H absorption band has not been detected spectroscopically.

The use of empirical formulae[10] to calculate the approximate frequency of the phosphoryl band can be helpful in interpretation provided that due care is taken. We have found that the formula gives reliable results, usually within 10 cm^{-1} of the observed frequency, except in the case of acids where the variable hydrogen bonding makes the assignment of an "electronegativity" to the OH group impracticable. The calculation must, however, be performed accurately if the result is to be useful. The value obtained from the formula for tricapryl phosphate is 1289 cm^{-1}, not 1176 as quoted.[8] For di-sec-butylphenylphosphonate it is 1266 cm^{-1} rather than 1307.[11]

Care should also be taken in applying correlations developed by other workers, particularly in ensuring that the original assignment is clearly understood. For example, the assignment of a band at 1375 cm^{-1} to an R—O—P vibration[12] on the stated authority of McIvor *et al.*[13] is unacceptable as there is no reason to vary McIvor's assignment of this band to a C—H deformation mode. Similarly the assignment of the 926 cm^{-1} band[14] to a ring vibration by analogy with the work of Cason *et al.*[15]



cannot be justified, since Cason's assignment is for rings involving P groups and the band used is due to a P—O—(C) vibration perturbed by the variation of bond angles on ring formation This correlation will obviously not be applicable to a ring such as



, with no P—O—C bonds.

Again, instead of attributing bands in the 715–770 cm^{-1} region to P—C vibrations as stated, Thomas[5] stated that this assignment[16] should be regarded with grave suspicion. There are further errors of this type in the paper, but to enumerate them in detail would be needlessly repetitious.

Differences between the authors' spectra and other published spectra may indeed in some cases be caused by variation in the impurity content. However, when making such comparisons, it must be realised that it can be misleading to compare spectra obtained from different physical forms of the material, *e.g.*, solutions and capillary films, since band positions and relative intensities vary unpredictably in solution, and even more markedly when a change of state is involved. Care should also be taken to ensure the chemical validity of the comparison, *e.g.*, the Sadtler[17] spectrum (No. 9041), quoted as a comparison for dibutyl hydrogenphosphonate, is, in fact, that of dibutyl hydrogen phosphate.

Finally, a word of warning should be given to other chemists who may be tempted to interpret infrared spectra solely on the basis of correlation tables. Correlations are derived by spectroscopists as a guide to the region in which absorption bands should appear if a specific group is present in the molecule. The reliability of a correlation will depend on the number of compounds on which it was based and on their variety. At best it will only be a guide to a region, at worst it may be a frequency for a single compound. It should always be applied logically. Because P—H compounds absorb in the region of 2400 cm^{-1} it does not follow[18] that all absorptions in this region must be due to P—H vibrations. In general, it is impossible to assign all the absorption bands of any complex organic molecule.

The recording of spectra under conditions designed to accentuate weak bands increases the difficulty of interpretation in many cases. Because an absorption band is weak it is not necessarily caused by an impurity; it may be an overtone or combination band. Unless a spectrum of the compound is available, taken under identical conditions, in which a particular band is absent, there is no certain way of identifying that band as being due to an impurity. If a specific impurity is suspected of being present, then its whole spectrum should be considered in relation to that of the material in which it is occurring. Thus, the assignment of the 2380 cm^{-1} band in tricapryl phosphate[2] to unreacted capryl alcohol is obviously incorrect if the relative intensity of this band and the OH band in the spectra of capryl alcohol are considered. In addition, visual estimation of the absorption intensity of this band would have shown that the intensity is greater in the spectrum of a 0·05-mm film of the phosphate, in which it is stated to be an impurity, than in a 0·2-mm film of the alcohol.

War Department
C.D.E.E.
Porton Down, Wilts., England
25 *September* 1961

L. C. THOMAS
ROSEMARY A. CHITTENDEN

REFERENCES

[1] C. A. Horton and J. C. White, *Talanta*, 1961, **7**, 215.
[2] *Idem, loc. cit.*, 218.
[3] *Idem, loc. cit.*, 222.
[4] L. C. Thomas and Rosemary A. Chittenden, in press.
[5] L. C. Thomas, *Chem. and Ind.*, 1957, 198.
[6] L. C. Thomas, Rosemary A. Chittenden and H. E. R. Hartley, in the press.
[7] C. A. Horton and J. C. White, *loc. cit.*, 217, 219, 220, 226, 229.
[8] R. B. Fox, U.S. Naval Research Lab., NRL 5242, 1959.
[9] G. O. Doak and L. D. Freedman, *Chem. Revs.*, 1961, **61**, 31.
[10] J. V. Bell, J. Heisler, H. Tannenbaum and J. Goldenson, *J. Amer. Chem. Soc.*, 1954, **76**, 5185.
[11] C. A. Horton and J. C. White, *loc. cit.*, 219.
[12] *Idem, loc. cit.*, 220.
[13] R. A. McIvor, G. A. Grant and C. E. Hubley, *Canad. J. Chem.*, 1956, **34**, 1611.
[14] C. A. Horton and J. C. White, *loc. cit.*, 225.
[15] J. Cason, W. N. Baxter and W. DeAcetis, *J. Org. Chem.*, 1959, **23**, 247.
[16] D. E. C. Corbridge, *J. Appl. Chem.*, 1956, **6**, 456.
[17] S. P. Sadtler, *Infrared Spectra*. Sadtler and Sons, Philadelphia.
[18] Aristotle, *Prior Analytics*, Book 1, Ch. 3 $^{a}40$–$^{b}3$, *circa* 350 B.C.

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EDITORIAL NOTE

SOME months ago we promised to give a brief account of our editorial and refereeing policy, and considerable interest has been expressed in this.

As is implied in our Notes for Contributors, our aim is to provide a journal in which the standard of the contributions is very high, giving satisfaction at the same time to our subscribers and our contributors. The methods which we use to attain this end will perhaps be best indicated by describing the processing of a typical contribution from receipt to publication.

On receipt, either by the Editor-in-Chief or one of the Regional Editors, a paper is acknowledged formally, and is sent with as little delay as possible (aiming at an interval of a few days at most) to a suitable referee. The Editor-in-Chief and the Regional Editors are all experienced analytical chemists, who are concerned to make the right choice of referee in the light of their familiarity with the field and their acquaintance with a wide circle of experts. This choice is dictated solely by the subject of the paper, and the aim is to choose an undoubted authority in the field, without regard to whether he is "academic" or "industrial." The referee form which accompanies the paper carries the following extracts from *Notes to Contributors*, as a guide to the quality to be looked for by the referee:

"Contributions may deal with any aspect of analytical chemistry, although papers concerned exclusively with limited fields already catered for by specialist journals should normally be directed to those journals, and should only be submitted to TALANTA if their analytical implications as a whole are such as to make their inclusion in a more general background desirable.

"Original papers, short communications, preliminary announcements and reviews will be published. Since TALANTA is an international journal, contributions are expected to be of a very high standard. Research papers should make a definite contribution to the subject. Special importance will be attached to work dealing with the principles of analytical chemistry in which the experimental material is critically evaluated and to similar fundamental studies. Reviews in rapidly expanding fields, and reviews of hitherto widely scattered material, will be considered for publication, but should be critical.

"Original papers, short communications and reviews will be refereed in the normal way. Referees will be encouraged to present critical and unbiassed reports which are designed to assist the author in presenting his material in the clearest and most unequivocal way possible. To assist in achieving this completely objective approach, referees will be asked to submit signed reports. At the discretion of the Editor-in-Chief, the names of referees may be disclosed if thereby agreement between author and referee is likely to result. Authors should appreciate that the comments of referees are presented in a constructive spirit, and that agreement between the views of author and referee must result in a higher standard of publication."

The questions asked of the referee are six in number, as follows:

1. Is the paper of sufficient interest and originality and is its subject matter suitable for it to be published in the Journal (subject to the alterations suggested in the following sections)
   (*a*) in the form of an original paper (or review)?
   (*b*) as a short communication?
2. If the paper is generally acceptable, are there any obvious errors of fact or logic—as distinct from points of scientific controversy or literary style—which need correction?
3. If the paper is too long, what sections could be abbreviated?
4. If the paper is obscure in any respect, what alterations or additions would remove the obscurity?
5. Have you any further suggestions for improvement?
6. Are there any parts of the paper to which you have been unable to give adequate consideration?

The referee is asked to report within two weeks, and, on the whole, referees are very co-operative in this respect—indeed, in all respects.

When the referee's report is received, any points of substance which he has made are forwarded to the author for his consideration. On the whole, the editorial view is that one of the principal functions of the referee (after the primary one of deciding the over-all value of the paper, of course) is to draw attention to matters which, in his view, may be the result of author-blindness. In many cases, therefore, it is regarded as sufficient if the criticisms of the referee are brought to the notice of the author, whether he accepts them or not. Often the author may be as eminent in his field of research as the referee, and in the event of disagreement, one is as likely to be correct as the other. The editor who would venture to assert that all his referees are right all the time, and that all his authors are wrong all the time, would indeed be bold (and, we suspect, unsuccessful).

It may well be that more than one triangular exchange of correspondence between editor and author and editor and referee is necessary before the paper is finally accepted for publication, but on the whole, where the paper has been regarded as worthy of publication, we have found a ready (and indeed grateful) acceptance by authors of the referee's criticisms, and an equally ready approval by referees of the author's revisions—or of his objections to the criticisms.

On acceptance, the paper is now ready to be prepared for the press. Diagrams must go to the publishers, in many cases for re-drawing, and thence to the block-makers. Copies of the summary must go to the translators. The manuscript must be corrected and marked up for press by the Editor-in-Chief or the Assistant Editor. This, we must sorrowfully note, is in many instances made no easier by the form in which the authors have submitted manuscripts. Papers often have to be cut in pieces and stuck together again to transfer summaries from end to beginning (or, in the case of short communications, *vice versa*). Lists of references frequently have to be retyped to transform them to the conventional form used by TALANTA. On the other hand, we must admit that a few of our contributors are so good in this respect that we suspect they have actually studied the Journal before preparing their manuscripts! These, alas, are still too much in the minority.

While on this topic, we would also beg contributors who are writing in a language not their own to have their papers checked before submission, if possible, by a technical colleague who writes the language fluently. This, we think, would often save the editors a considerable amount of re-writing, and the printers a considerable amount of heart-burning at the futuristic mixture of red and black which is presented to them. In all justice to our printers, it is very rarely that they have admitted defeat; and the number of times that the editor has been complimented by authors on the "clean" proofs is a clear indication of how successfully the printers are doing their job.

In order to save time, papers are normally now set directly in page form. It is, therefore, no help if an author decides at this stage that two paragraphs of additional explanation or a new Table are necessary. Alterations, in fact, should be kept to the bare minimum. Even the addition of a footnote may alter the pagination of the whole paper.

By the time that the proofs are received from the printer, the block proofs should also be ready. Once again, any alteration may and indeed almost certainly will involve time and money in the preparation of a new block. Proofs are corrected by a

team of voluntary readers in addition to the author. Most authors having returned a proof marked "No corrections are necessary," would probably be surprised to find how many errors or inconsistencies they have missed, and how much red ink is on the proof by the time that it goes to the printers for final correction before printing.

Finally, we would point out that we have a "deadline" with the printers, a date by which the corrected and made up proofs must be returned. If the proof of your paper sits on your desk for a week, this may make all the difference between appearing in the forthcoming issue or being held over to the next.

The first issue of TALANTA appeared in mid-1958. We think we have learned (the hard way) many of the snags in editing and producing it. We are grateful to those authors and referees whose patience, in our teething stage, have made us feel that this is a worthwhile venture, and we look forward to repaying this patience by providing the best possible service both for our contributors and our readers.

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PUBLISHER'S ANNOUNCEMENT

Special Subscription Rate for Students

THE publishers are pleased to announce a special Student's Rate for *Talanta*. *Bona fide* students will be able to obtain the Journal for £3.10.0. (U.S.A. $10) per annum. This offer is intended to encourage young people to follow the latest literature and to start building their personal libraries.

Students wishing to take advantage of this special subscription rate should send their application, with their remittance, to the Subscription Department of either the Oxford or New York Office of Pergamon Press (addresses are given on the inside cover of the Journal). The application should be accompanied by a brief note from their professor or tutor to the effect that the individual is a *bona fide* student.

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NOTICES

The Commission on *Microchemical Techniques, Section of Analytical Chemistry*, **International Union of Pure and Applied Chemistry,** has recently recommended a series of test substances for the microdetermination of nitrogen in organic compounds (see *Pure and Applied Chemistry*, 1961, **3,** 513).

FRANCE

Les conférences suivantes auront lieu à la Faculté de Pharmacie, Paris, à l'amphithéâtre Bourquelot, à 17 h 45, sous la direction des Professeurs J. A. GUATIER et P. MALANGEAU:

Mardi 13 *février* 1962: **Les anthocyanes des fruits—méthodes d'identification et applications:** Professeur P. RIBEREAU-GAYON.

Mardi 27 *février* 1962: **De la distillation à la chromatographie:** Professeur P. JAULMES.

Jeudi 15 *mars* 1962: **Les réactions électrochimiques dans l'acétonitrile—aspects récents de l'oxydation à une électrode de platine:** Mme. J. BADOZ-LAMBLING.

Mardi 27 *mars* 1962: **La diazocpulation en analyse organique:** M. J. Bartos.

UNITED KINGDOM

Thursday 18 *January* 1962: **Polarography of Carbon Dioxide:** Professor J. JORDAN: *Polarographic Society*. Biochemical Department, Institute for Diseases of Chest, Brompton Road, London, S.W.3. 5.00 p.m.

Thursday 8 *February* 1962: **New Analytical Reagents in Colorimetric Analysis:** *Society for Analytical Chemistry*. London 2.30 p.m.

Wednesday 14 *February* 1962: **Automatic Methods in the Analytical Laboratory:** Dr. I. D. P. WOOTTON and Dr. G. MATTOCK: *Society for Analytical Chemistry, Midlands Section and Association of Clinical Biochemists*. University, Edgbaston, Birmingham, 15. 6.30 p.m.

Wednesday 21 *February* 1962: **Assessment of Antibiotics in Animal Feeds:** *Society for Analytical Chemistry, Biological Methods Group*. Burlington House, London, W.1. 7.00 p.m.

Thursday 22 *February* 1962: **Analytical Research:** Dr. J. HASLAM: *Society for Analytical Chemistry, Midlands Section*. Technical College, Luton. 6.30 p.m.

Friday 23 *February* 1962: **Annual General Meeting** followed by reading of Original Papers: *Society for Analytical Chemistry, Microchemistry Group*. Burlington House, London, W.1. 6.45 p.m.

Friday 23 *February* 1962: **Death from Poison,** Dr. A. C. HUNT, and **Scientific Aspects of Crime Detection,** Detective Supt. J. K. MCLELLAN: *Society for Analytical Chemistry, Scottish Section*. Royal Society of Edinburgh, George Street, Edinburgh. 7.15 p.m.

Tuesday 27 *February* 1962: **Some Surface Effects in Electro-analytical Chemistry:** Professor H. A. LAITINEN: *Society for Analytical Chemistry, Physical Methods Group* and *Polarographic Society*. School of Pharmacy, London, W.C.1. 6.30 p.m.

Wednesday–Saturday 28–31 *March* 1962: **Conference on Molecular Spectroscopy:** *Institute of Petroleum, Hydrocarbon Research Group*. William Beveridge Hall, Senate House, University of London, W.C.1 (see also *Talanta*, 1961, **8,** 695).

The provisional programme is as follows:

Wednesday 28 *March*

H. W. THOMPSON (University of Oxford, U.K.)	*Trends in Chemical Applications of Spectroscopy.*
A. WALSH (C.S.I.R.O., Melbourne, Australia)	*Atomic Absorption Spectroscopy.*

Thursday 29 *March*

R. E. RICHARDS (University of Oxford, U.K.)	*New Development in Magnetic Resonance Spectroscopy.*
R. B. WILLIAMS (Humble Oil & Refining Co. Texas, U.S.A.)	*A study of Nuclear Magnetic Resonance Performance Parameters.*
D. J. E. INGRAM (University College of North Staffs., U.K.)	*The Method and Technique of Electron Resonance, and its Application to Metal Complexes.*
D. H. WHIFFEN (N.P.L., U.K.)	*A Review of Electron Spin Resonance of Organic Radicals.*
R. N. DIXON (University of Sheffield, U.K.)	*Free Radical Spectroscopy.*
T. M. SUGDEN (University of Cambridge, U.K.)	*Spectrophotometry of Free Radicals in Flames.*

Friday 30 *March*

G. R. WILKINSON (University of London, U.K.)	*Spectroscopy in the Far Infrared.*
N. SHEPPARD (University of Cambridge, U.K.)	*Infrared Spectra of Molecular Rotations in Condensed States.*
L. J. BELLAMY (ERDE, Waltham Abbey, U.K.	*The Effect of Internal Environment on Group Frequencies.*
H. W. THOMPSON (University of Oxford, U.K.)	*Factors Affecting Characteristics of Infared and Raman Vibrational Bands.*
VAN ZANDT WILLIAMS (Perkin-Elmer Corpn., U.S.A.)	*Developments in Applied Spectroscopy.*
H. E. HALLAM (University College of Swansea, U.K.)	*Solvent Effects in Infrared Spectra.*

Saturday 31 *March*

W. C. PRICE (University of London, U.K.)	*Vacuum Ultraviolet Spectra and Photoionisation of Molecules and Radicals.*
A. D. WALSH (University of St. Andrews, U.K.)	*Electronic Spectra of Small Polyatomic Molecules.*

Contributions to the conference will also be given by:

C. W. CHANTRY (N.P.L., U.K.)	*Optical Absorption Spectra of Orientated Free Radicals.*
R. L. WARREN (Middlesex Hospital, U.K.)	*A Versatile Micro-sample Flame Spectrophotometer.*
D. M. ADAMS (I.C.I. Ltd., The Frythe, U.K.)	*Solvent Effects on the Infrared Spectra of Inorganic Complexes.*

It is also intended, during the conference, to discuss other topics, such as X-ray fluorescence.

April or May 1963: **Symposium on the Analysis of Calcareous Materials:** *Society of Chemical Industry, Road and Building Materials Group*, London.

It will include analytical procedures, using either chemical or physical methods for the determination of elements, radicals or compounds in naturally occurring or artificially made materials consisting to a large extent of calcium compounds. Thus, it will cover the analysis of calcareous rocks and minerals, hydraulic cements, lime, whiting, gypsum plasters, slags, calcareous building materials and some ceramic products. Papers will be contributed on physical methods of analysis such as spectrometry, flame photometry, X-ray fluorescence, X-ray diffraction, and mass spectrometry as well as chemical methods.

It is intended that the Proceedings of the Symposium shall be in such a form as to serve as a text book of analysis for this field. Authors who wish to contribute papers on appropriate topics for this Symposium are invited to write for further information to the Symposium Secretary: Mr. G. E. BESSEY, Chalk Lime and Allied Industries Research Association, Church Street, Welwyn, Herts., England. It will be necessary for manuscripts to be available by October, 1962.

The *Annual General Meeting* of the *Physical Methods Group of the Society for Analytical Chemistry* was held at Burlington House, London, W.1, on Tuesday, 21 November, 1961. The Chairman of the Group, Dr. G. W. C. MILNER, presided.

The following were elected Officers of the Group for the forthcoming year:

Chairman: Dr. W. CULE DAVIES

Vice-Chairman: Mr. L. BREALEY

Hon. Secretary and Treasurer: Dr. T. L. PARKINSON, Product Research Division, Beecham Foods Ltd., Harpenden Rise, Harpenden, Herts.

The following new British Standards have recently been announced (see *B.S.I. News*, 1961, December):

B.S. 3420: 1961: *Sealed glass cells for photometric haemoglobinometry.* This specifies requirements for sealed glass cells with suitable solutions for the accurate determination of haemoglobin concentration of blood samples, and describes the methods of using such samples to calibrate clinical instruments for the estimation of haemoglobin. (*Price* 4s.)

B.S. 3430: 1961: *Method for the sampling of paper for testing.* This specifies a method of obtaining a representative sample of a lot of paper for most test purposes. It applies to substances below 250 g/m^2 and is identical, except for editorial adjustments, with ISO Recommendation R 186. (*Price* 4s.6d.)

B.S. 3431: 1961: *Method for the conditioning of paper and board test samples.* This defines the conditioning atmosphere and the method of conditioning paper and board before and during testing. Except for minor (chiefly editorial) adjustments it is identical with ISO Recommendation R 187. (*Price* 3s.)

B.S. 3432: 1961: *Method for the determination of paper substance.* This specifies methods for determining the substance (*i.e.* weight of a specified area) of paper, under three different conditions, *viz.* 'as taken', 'after conditioning' and 'on the oven dry basis'. (*Price* 4s.6d.)

B.S. 3433: 1961: *Methods for the sampling and testing of paper for moisture content.* This specifies two methods of determining moisture content. Part I deals with the oven drying method and applies to papers that do not contain appreciable quantities of materials, other than water, which will escape from the paper at the test temperature. Part 2 specifies an entrainment distillation method for materials which cannot be tested by the oven-drying method owing to the probable loss of volatile or fusible constituents. (*Price* 5s.)

The following Amendment Slips are also announced;

B.S. 700: 1952: *Graduated pipettes and one-mark cylindrical pipettes.* Amendment No. 3: PD 4325.

B.S. 1017: *The sampling of coal and coke: Part* 2: 1960: *Sampling of coke.* Amendment No. I: PD 3266.

B.S. 1428: *Microchemical apparatus: Part JI:* 1954: *Micro-electrolytic apparatus.* Amendment No. I: PD 4350.

B.S. 2782: *Methods of testing plastics: Part* 4: *Analytical methods and viscosity in solution.* Amendment No. 7: PD 4364: Methods 402: Analysis of water extract of phenolic mouldings.

UNITED STATES OF AMERICA

Thursday–Friday 25–26 *January* 1962: **Ninth Annual Western Spectroscopy Conference.** Asilomar, Pacific Grove, Calif.

Monday 29 *January–Thursday* 1 February 1962: **Fifteenth Annual Symposium on Modern Methods of Analytical Chemistry.** Louisiana State University, Baton Rouge, La.

The following programme of invited speakers has been arranged:

EPR in investigation of Electrode Processes.	RALPH ADAMS (University of Kansas, U.S.A.)
The Electron Probe.	L. S. BIRKS (Naval Research Laboratory, U.S.A.)
Chronopotentiometry.	DONALD DAVIS (Louisiana State University, U.S.A.)
Fusion Reactions and Morphological Structure of Precipitates.	L. ERDEY (Technical University of Budapest, Hungary)
Raman Spectroscopy and Infrared Spectroscopy.	R. NORMAN JONES (National Research Council, Canada)
Detector Systems for GLC.	KURT KRAUS (Oak Ridge National Laboratories, U.S.A.)
Analysis of High Polymers.	JOHN MITCHELL (E.I. du Pont de Nemours & Co. Ltd., U.S.A.)
Activation Analysis.	W. W. MEINKE (University of Michigan, U.S.A.)
Atomic Absorption Spectroscopy.	ALAN WALSH (C.S.I.R.O., Australia)

Monday–Friday 5–9 *February* 1962: **A.S.T.M. Committee Week.** Statler Hilton and Sheraton-Dallas Hotels, Texas.

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PAPERS RECEIVED

An investigation of 5-(3-nitrophenylazo)-salicylic acid (Na salt) as a spectrophotometric reagent for magnesium. D. BETTERIDGE and JOHN H. YOE. (30 *October* 1961).

The flame photometric determination of titanium. C. L. CHAKRIBARTI, W. F. PICKERING and C. L. WILSON. (30 *October* 1961).

Titrimetric determination of vanadium^{IV} with cerium^{IV} sulphate at room temperature, using rhodamine 6G as fluorescent indicator. G. GOPALA RAO and L. S. A. DIKSHITULU. (3 *November* 1961)

Reductometric titration by ferrous sulphate in a medium of triethanolamine—I. Determination of manganese. JAN DOLEZAL, STANISLAV ROSSLER and JAROSLAV ZYKA. (7 *November* 1961)

Über die analytische Gruppe fur Ti(IV) in organischen Reagentien. L. SOMMER. (10 *November* 1961).

Analytical potential of separations by liquid ion-exchange. C. F. COLEMAN, C. A. BLAKE, JR., and K. B. BROWN. (13 *November* (1961).

The use of oxycellulose for the collection of traces of metals. E. SCHULEK, ZS. REMPORT-HORVATH and A. LASZTITY. (14 *November* 1961).

Mixed chemiluminescent indicators. L. ERDEY, W. F. PICKERING and C. L. WILSON. (20 *November* 1961).

Some observations on the precipitation of niobium and tantalum from homogeneous solution. T. H. RICHERT and LOUIS GORDON. (20 *November* 1961).

Ion-exchange separations using sulphosalicylic acid. JAMES S. FRITZ and THOMAS A. PALMER. (20 *November* 1961).

Some consideration on masking effectiveness. ADAM HULANICKI. (23 *November* 1961).

The analytical use of a standard solution of iodine trichloride. E. SCHULEK and L. LADANYI. (23 *November* 1961).

Thiourea and its organic derivatives—I: Oxidimetric determination with potassium iodate. BALWANT SINGH and BALBIR CHAND VERMA. (23 *November* 1961).

The determination of gallium. G. R. E. C. GREGORY and P. G. JEFFERY. (29 *November* 1961).

The colorimetric determination of molybdenum with polyhydric phenols. H. BUCHWALD and E. RICHARDSON. (28 *November* 1961).

Emission spectra from high-frequency excitation—III: A study of argon-carbon dioxide mixtures. C. L. CHAKRIBARTI, R. J. MAGEE and C. L. WILSON. (28 *November* 1961).

Analytical rapid methods for the determination of metals and inorganic materials—XIII: The determination of tin in metallic antimony. ZDENĚK ŠULCEK, JAN DOLEŽAL, JAN MICHAL, VÁCLAV SYCHRA. (29 *November* 1961).

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APPLICATIONS DE LA CHELATOMETRIE—XV*

DOSAGE VOLUMETRIQUE DU 6-PURINETHIOL

CLAUDE HENNART
Seraincourt, Seine et Oise, France

Résumé—La 6-Mercaptopurine ou 6-purinethiol, peut être dosée par chélatométrie après une précipitation au moyen du nitrate d'argent; l'excès de celui-ci est dosé, après filtration, par l'acide éthylènediamino-tétracétique en présence de tétracyanonickelate de potassium et de murexide.

(*Received* 16 *June* 1961. *Accepted* 28 *June* 1961)

INTRODUCTION

DANS un travail en collaboration avec E. Merlin[1] sur la synthèse de la dichloro 4–6 pyrimidine, nous indiquions l'importance prise par les dérivés de la pyrimidine dans la recherche des produits à activité antitumorale, ceci en raison, sans doute, de la préférence marquée par les tissus cancéreux pour l'uracile dans la synthèse de leurs acides nucléïques.[2,3] Une substance particulièrement intéressante pour le traitement des leucémies aïgues est certainement la 6-mercaptopurine ou 6-purinethiol[4–15] facilement obtenue à partir de la 6-hydroxypurine.[16]

La 6-mercaptopurine est capable de fixer, par substitution, deux atomes d'argent, l'un sur la partie iminazolique de sa molécule et l'autre sur sa fonction thiol; Blazek et Stejskal[17] en ont déduit, en 1956, un procédé de dosage argentométrique: après une précipitation en milieu ammoniacal par une solution décinormale de nitrate d'argent suivïe d'une filtration, l'argent en excès dans le filtrat est titré par la méthode courante au thyocyanate d'ammonium en présence d'ions ferriques. Nous nous sommes inspirés de ce procédé pour établir une méthode chélatométrique basée sur le dosage de l'argent selon Flaschka et Huditz;[18,19] nous avions déjà utilisé avec satisfaction ce mode de dosage dans le cas des halogènes organiques,[20,21] et de diverses sulfamides:[22] en présence de tétracyanonickelate de potassium, l'argent prend, dans ce complexe, la place du nickel et on dose celui-ci, en milieu ammoniacal, par l'acide éthylène diaminotétracétique en présence de murexide comme indicateur.

PARTIE EXPERIMENTALE

Réactifs utilisés

Ammoniaque: 10%

Nitrate d'argent: 0,05*M*

Tétracyanonickelate de potassium: 0,025*M*: on dissout 6,25 g d'acétate de nickel, $(CH_3COO)_2Ni$, $4H_2O$, dans 300 ml d'eau distillée, puis ajoute 100 ml d'ammoniaque et 10 mg de murexide; à cette solution, on ajoute, jusqu'à virage précis au violet, une solution contenant 6,2 g de cyanure de potassium dans 500 ml d'eau distillée (on procède d'abord par approximation sur les 9/10ème de la solution nickelique et termine à la burette après avoir ajouté le dernier dixième de cette solution); on complète le tout à un litre au moyen d'eau distillée.

Chélate: 0,01*M*: nous avons appelé ainsi une solution préparée par dissolution de 3,7 g d'éthylène-diaminotétracetate disodique dans un litre d'eau fraîchement bouillie et distillée; on détermine

* Articles précédents: XIII—*Chim. Analyt.*, 1961, (sous presse); XIV—*Analyt. Chim. Acta*, 1961, **25**, 21.

la molarité de cette solution à partir d'un poids connu de magnésium ou de zinc métalliques chimiquement purs en utilisant le noir-ériochrome T comme indicateur ou à partir d'une solution titrée de nitrate d'argent en présence du réactif ci-dessus et de murexide.

Murexide: 1%: on pèse 0,1 g de murexide, ajoute 10 g de chlorure d'ammonium bien sec et broye le tout intimement.

Mode opératoire

On pèse un poids p supposé contenir 50 mg qu'on dissout dans 10 ml d'eau et 3 ml d'ammoniaque 10%; on ajoute 25 ml de nitrate d'argent 0,05M, agite pendant quelques minutes et complète à 100 ml au moyen d'eau distillée; on agite et filtre; on prélève 25 ml du filtrat auxquels on ajoute 25 ml de tétracyanonickelate de potassium 0,025M, 25 ml d'ammoniaque 10% et quelques décigrammes de murexide 1%; on verse le chélate 0,01M au moyen d'une burette de 10 ml jusqu'au virage au violet.

Le titre % calculé en Purinethiol anhydre est donné par la formule:

$$T_{\%_p} = \frac{V \times 7{,}609}{p}$$

où $V = (25 \times N'_A) - (8 \times N'_C \times V')$

V' = nombre de ml de chélate utilisé

N'_C = molarité de ce réactif

N'_A = molarité du nitrate d'argent

p est exprimé en grammes

Le titre % calculé en monohydrate peut être obtenu en remplaçant le nombre 7,609 par le nombre 8,51 dans la formule précédente.

RESULTATS OBTENUS

p en *mg* (produit anhydre)	titre trouvé, %	déviation, %
47,2	99,2	−0,8
46,4	100,3	+0,3
49,3	99,5	−0,5
53,2	99,1	−0,9
51,7	100,5	+0,5
48,8	99,4	−0,6

Summary—6-Mercaptopurin, or 6-purinthiol, can be precipitated by means of standard silver nitrate solution, the excess of which is determined, in the filtrate, chelatometrically.

Zusammenfassung—6-Mercaptopurin, oder 6-purinthiol, werden dann mit Silbernitratlösung bekannter Normalität gefällt, deren Überschuss im Filtrat chelatometrisch bestimmt wird.

BIBLIOGRAPHIE

[1] C. Hennart et E. Merlin, *Bull. Soc. Chim. France*, 1959, 741.
[2] R. J. Rutman *et coll. Cancer Res.*, 1954, **14**, 119.
[3] K. C. Leibman et C. Heidelberger, *Federation Proceedings*, 1955, **14**, 243.
[4] K. Sugiura *et coll., Cancer Research*, 1950, **10**, 178.
[5] D. A. Clarke *et coll., ibid.*, 1953, **13**, 593.
[6] C. T. Bahner *et coll., J. Amer. Chem. Soc.*, 1953, **75**, 6301.
[7] G. B. Elion *et coll., J. Biol. Chem.*, 1953, 202, 647.
[8] J. H. Burchenal *et coll., Blood*, 1953, 8, 965.
[9] G. B. Elion *et coll., J. Biol. Chem.*, 1953, 204, 35.
[10] H. E. Skipper *et coll., Cancer Research*, 1954, **14**, 294.
[11] K. H. Schmidt, *Arzneimittel Forsch.*, 1954, **4**, 146.

[12] J. Bernard et M. Seligmann, *Sem. Hopitaux*, 1954, **30,** 2971.
[13] J. Bernard, *Le Sang*, 1954, **25,** 840.
[14] F. de Carli, *Giornale Italia di Chemoterapia*, 1956, **3,** (n° 1-2).
[15] R. Latarjet, *Rev. Hematol.*, 1956, **11,** n° 2.
[16] G. B. Elion, E. Burgi et G. Hitchings, *J. Amer. Chem. Soc.*, 1952, **74,** 411.
[17] J. Blazek et Z. Stejskal, *Ceskosl. Farm.*, 1956, **5,** 27.
[18] H. Flaschka et F. Huditz, *Z. Analyt. Chem.*, 1952, **137,** 104.
[19] H. Flaschka, *Mikrochemie*, 1953, **40,** 21.
[20] C. Hennart, *Mikrochim. Acta*, 1961, 543.
[21] *Idem, Peint. Pigm. Vernis*, 1961, 37, 557
[22] *Idem, Chim. Analyt.*, 1961, 37 557.

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PHOTOMETRIC DETERMINATION OF SCANDIUM WITH α-(2,4-DIHYDROXYPHENYLAZO)-PYRIDINE*

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Summary—Under certain conditions the scandium ion gives a characteristic coloration with α-(2,4-dihydroxyphenylazo)-pyridine on interaction with it in the molar ratio 1 : 1. A photometric method has been worked out for the determination of 0·05–2 μg of Sc/ml using this reagent. Be, Mo, Ca, Mg do not interfere with the determination, but Zn, Co, Ni, Cd, Cu, Tl, In, Ga, Zr, Th, U and Fe do.

FEW colour reactions and photometric methods are known for the determination of scandium.[1–5] This study was aimed at an examination of the possibility of carrying out the photometric determination of scandium by means of α-(2,4-dihydroxyphenylazo)-pyridine (DPP), which has in recent years been introduced widely in analytical chemistry as a complexometric indicator.

EXPERIMENTAL

Reagents

Standard scandium solution: Prepared by dissolving an accurately weighed amount of spectrally pure scandium oxide in hydrochloric acid. Its concentration was equal to $1{\cdot}589 \times 10^{-3}M$.

α-(2,4-*Dihydroxyphenylazo)-pyridine* (*DPP*) *solution:* Prepared by dissolving a pure preparation of the base (m.p. 185–6°) in a dilute solution of caustic soda and diluting with water. To the solution obtained hydrochloric acid was added until the reaction was neutral to universal indicator paper. A DPP solution having a concentration of $1{\cdot}589 \times 10^{-3}M$ used for titrations was prepared by accurate weighing. To attain the desired pH a 20% aqueous solution of ammonium acetate was used.

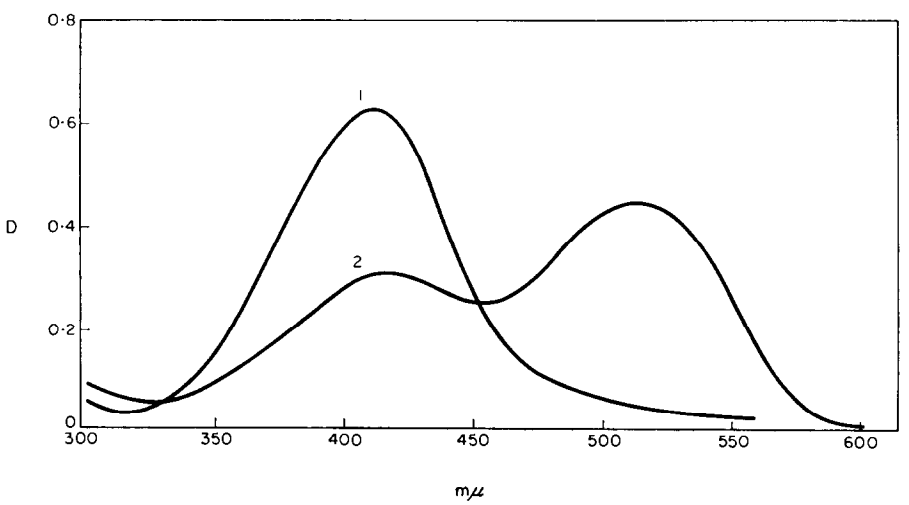


Fig. 1—Absorption curves (spectrophotometer SF-4; 1-cm cell; optical density referred to water):
1-Solution of DPP at pH 6·22; 2-Complex of scandium with DPP at pH 6·12.

* Translated from the Russian: *Vestnik Mosk. Univ., Ser. Khim.* 1960, No. 6, 46.

Complex of scandium with α-(2,4-dihydroxyphenylazo)-pyridine

The scandium ion reacts with DPP forming a soluble compound having an intensely red colour. At relatively high concentrations of the scandium salt a flocculent precipitate separates out. The colour is stable with time, the optical density of the solutions undergoing no decrease on standing. The absorption curve of the solution of the compound formed was obtained in the presence of an excess of scandium. The solution contained $1{\cdot}27 \times 10^{-4}M$ scandium and $1{\cdot}66 \times 10^{-5}M$ DPP, the pH of the solution being adjusted to a value of 6·12 by a pH meter with a glass electrode. The optical density was measured on a spectrophotometer (CF-4) using a 1-cm cell, with reference to water. The absorption curve (Fig. 1) exhibits two maxima, at 420 mμ and at 515 mμ. The absorption curve of the reagent at the same concentration and pH 6·22 has one maximum at 410 mμ. The reagent solution absorbs only very slightly at 515 mμ. In the photometric determination of scandium the optical density at this wavelength must be measured with reference to a blank solution prepared by the same method but without the addition of scandium.

The molar ratio in the reaction of the scandium ion and DPP was determined by the isomolar series method. The constant overall concentration of scandium and the reagent was $6{\cdot}36 \times 10^{-5}M$; the concentration of scandium varied within the limits of $6{\cdot}36 \times 10^{-6}$ to $5{\cdot}72 \times 10^{-5}M$ and that of the reagent from $5{\cdot}72 \times 10^{-5}$ to $6{\cdot}36 \times 10^{-6}M$. The optical density of the solutions was determined at 515 and 550 mμ with reference to water. For the optical density at 515 mμ, a correction was introduced for the absorption by the reagent itself (curve 3, Fig. 2).

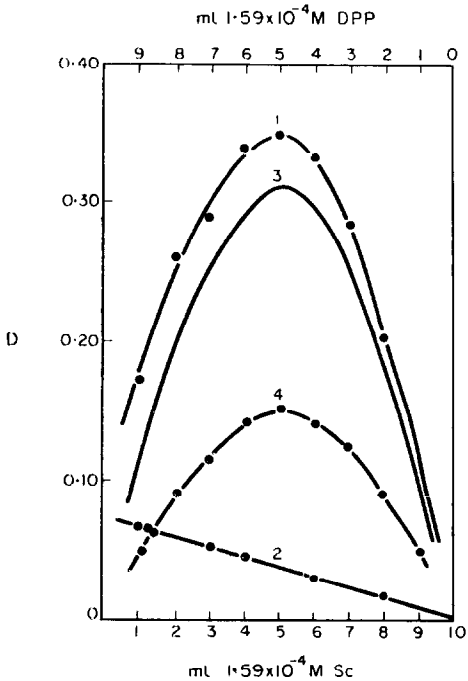


Fig. 2—Molar absorption in the interaction of the scandium ion with DPP by the method of isomolar media
1-Measured values of the optical density at 515 mμ referred to water; 2-Optical density of the corresponding solutions of DPP at 515 mμ referred to water; 3-Difference between curves 1 and 2; 4-Measured values of the optical density of isomolar solutions of a scandium salt and DPP at 550 mμ, referred to water.

The remaining conditions were identical with those employed in deriving the calibration curve (*cf.* below). On the curves (Fig. 2), the optical density maximum appears at a molar ratio of scandium to the reagent equal to 1 : 1. The position of the maximum reflects a fairly strong dissociation of the compound formed under the conditions of the experiment.

To verify the molar ratio found, the influence exerted by an excess of each of the components on the displacement of the equilibrium was studied. The formation of a compound with molar ratio 1:1 may be represented by the following reaction scheme:

$$ScO^+ + HP \rightleftarrows ScOP + H^+ \quad (1)$$

where HP = DPP. In this case an excess of scandium and an excess of the reagent must displace the equilibrium to an identical extent for a constant hydrogen ion concentration. If scandium does not react with the reagent in a molar ratio of 1:1 but 1:2 or any other ratio, equal excesses of either components will not exert the same influence on the displacement of the equilibrium. When the ratio of scandium:reagent is equal to 1:2, a change in the excess concentration of scandium by a factor of 10 must change the ratio (ScOP):(ScO^+) by $\sqrt{10}$, *i.e.* by 3·1 times, while a change in the excess concentration of the reagent by a factor of 10 must change the ratio in question by a factor of 10^2, *i.e.* 100. Two series of solutions were prepared as when deriving the calibration curve, one series of solutions containing 0·2 ml of a $1{\cdot}59 \times 10^{-3}M$ solution of scandium and 0·2, 0·4, 0·7, 1·6 and 3·0 ml of a $1{\cdot}59 \times 10^{-3}M$ solution of the reagent, and the other series containing 0·2 ml of a $1{\cdot}59 \times 10^{-3}M$ solution of the reagent and 0·2, 0·4, 0·8, 1·6 and 3·0 ml of a $1{\cdot}59 \times 10^{-3}M$ solution of scandium.

The right branch of the curve shown in Fig. 3 illustrates the change in the optical density of the solutions of the first series and the left branch refers to the solution of the second series.

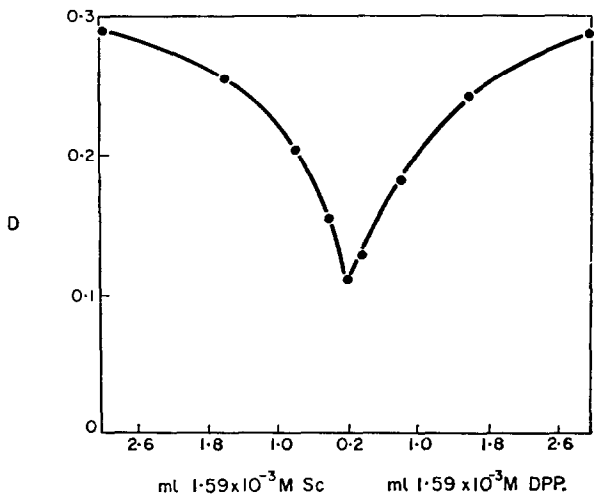


Fig. 3—The influence of an excess of scandium salt or of DPP on the optical density of solutions of the compound formed.

The figure clearly shows that an excess of either component influences the displacement of the equilibrium to an equal extent so that they evidently react in a molar ratio of 1:1.

The molar absorption coefficient of the solutions of the scandium compound formed was determined at 515 mμ. The solutions were prepared as for the derivation of the calibration curve, they contained acetate ions. The concentration of scandium was constant ($2{\cdot}54 \times 10^{-5}M$). The solutions contained different amounts of excess DPP (15 ml, 13 ml and 10 ml of a 0·01 % solution of the reagent). The molar absorption coefficients calculated for each solution were, respectively, equal to $2{\cdot}26 \times 10^4$, $2{\cdot}26 \times 10^4$, $2{\cdot}3 \times 10^4$ and $2{\cdot}14 \times 10^4$, giving an average value of $2{\cdot}21 \times 10^4$.

The results of the calculations relating to the equilibrium constants of reaction (1) are shown in Table 1.

The concentration of the complex was calculated from the equation

$$C_{comp} = D/l\Sigma,$$

where Σ is the molar absorption coefficient of the complex, l the thickness of the solution layer and D the measured optical density.

TABLE I—EQUILIBRIUM CONSTANT OF REACTION (1) AT 19° AND pH 5·95.

Total concentration C_{tot} mol/l $\times 10^{-5}$		Molar ratio of Sc : DPP	D^{515} (l = 1 cm)	Concn. of the complex $C_{comp} \times 10^{-5}$	Concn. of the free components $C_f \times 10^{-5}$		Equilibrium constant,* $K \times 10^{-2}$
Scandium	DPP				Scandium	DPP	
1·27	1·27	1:1	0·110	0·50	0·77	0·77	9·4
3·18	3·18	1:1	0·350	1·60	1·58	1·58	7·2
2·54	2·54	1:1	0·230	1·05	1·49	1·49	5·3
1·27	1·27	1:1	0·110	0·50	0·77	0·77	9·4
2·54	1·27	2:1	0·155	0·71	1·83	0·56	7·7
5·08	1·27	4:1	0·206	0·94	4·14	0·33	7·7
1·27	5·08	1:4	0·200	0·91	0·36	4·17	6·8

* Average $7{\cdot}6 \times 10^{-2}$

The concentrations of free scandium and reagent were found from the difference between the total concentrations and those parts of them which are bound in the complex. The apparent equilibrium constant of the reaction at pH 5·95 is equal to $7{\cdot}6 \times 10^{-2}$ (mean value of 8 results). It shows that the complex formed between scandium and the reagent under the conditions of the experiment is not very stable.

The apparent constant makes it possible to calculate the excess of reagent necessary for the spectrophotometric determination of scandium. It was found that more than a six-fold molar excess of the reagent must be present in the solution to ensure that 90% of the scandium is bound in the red coloured complex, and to raise this level to 99%, a sixty-fold molar excess of the reagent is required. Thus, in the photometric determination of scandium large amounts of the reagent must be employed. This result finds experimental confirmation.

Fig. 4 shows that the maximum development of the colour of the complex is only observed when the solution contains a greater than six-fold molar excess of the reagent with respect to the scandium.

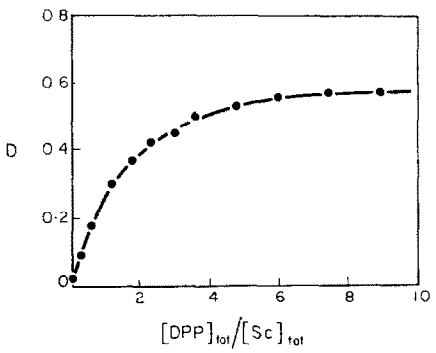


Fig. 4—Influence of an excess of DPP on the optical density of solutions of the scandium compound.

To carry out these experiments 0·4 ml of a $1{\cdot}59 \times 10^{-3}M$ solution of scandium and different volumes of a 0·01% solution of the reagent were used (the remaining conditions were as in the derivation of the calibration curve).

In clarifying the optimum pH values of the solution in the photometric determination of scandium, the experiments were carried out in the following manner: 2·0 ml of a $1{\cdot}59 \times 10^{-4}M$ solution of scandium and 1·0 ml of an 0·05% and the the reagent are introduced into a 50-ml volumetric as flask, 30–40 ml of water are added solution of pH of the solution is adjusted to the desired value determined by means of universal indicator paper, by the addition of sodium hydroxide or hydrochloric acid. The solution is then made up to the volume with water, and its pH is checked by means

of a glass electrode. The optical density of the solutions obtained is determined at 515 mμ with respect to water (Fig. 5). In the same manner a solution of DPP of identical concentration (without scandium) is prepared and its optical density is determined with respect to water (curve 2, Fig. 5).

These experiments showed that the optimum pH value of the solution for the photometric determination of scandium lies within the pH range 6 to 7·3. The optical density is thereby independent of the pH of the solution. To obtain the required medium it is recommended that a 20% solution of ammonium acetate be added. The best results are obtained by the addition of 2·5 ml of 20% ammonium acetate solution per 25 ml of the final solution.

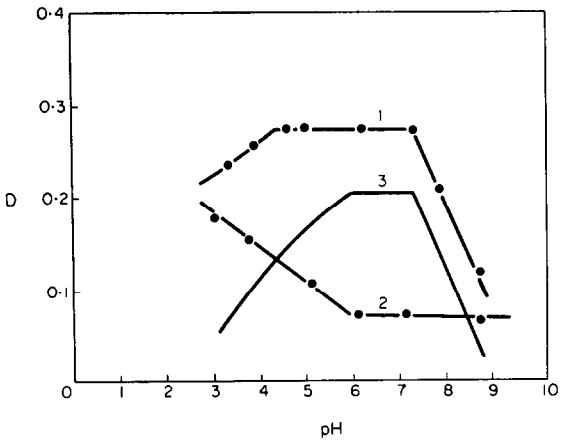


Fig. 5—Optimum pH value of the solution in the spectrophotometric determination of scandium by means of DPP:
1-Scandium compound in the presence of an excess of the reagent; 2-Reagent; 3-Difference between the curves 1 and 2.

Calibration curve

Twelve ml of neutral standard solution of scandium salt, of a concentration such that the final solution (after dilution to 25 ml) contains 0·05–2·0 μg of scandium/ml, is placed in a 25-ml volumetric flask. 2·5 ml of 20% ammonium acetate solution is added, followed by 2·0 ml of a 0·05% solution of the reagent. The solution is made up to the mark with water, well mixed and the optical density is measured at 515 mμ on a spectrophotometer using a 1-cm cell with reference to a solution prepared in the same way but without the addition of scandium. The solutions follow Beer's law within the limits of 0·05–2·0 μg of scandium/ml.

Interferences

Zinc, cobalt, nickel, cadmium, copper, thallium, indium, gallium, zirconium, thorium, uranium, iron and aluminium interfere with the determination of scandium either by forming coloured solutions or a coloured precipitate when the reagent is added. Beryllium, molybdenum, calcium and magnesium do not interfere (Table II). Thus, DPP is not a selective reagent for scandium.

TABLE II—DETERMINATION OF SCANDIUM IN THE PRESENCE OF OTHER ELEMENTS (29 μg OF SCANDIUM PRESENT)

Foreign ion, μg	Be 50	Mo 50	Ca 50	Ca 25	Mg 50	Mg 26
Sc found, μg	28	29	29	28	28	30
Error, μg	−1	0	0	−1	−1	+1

CONCLUSIONS

The scandium ion gives a characteristic coloration with α-(2,4-dihydroxyphenylazo)-pyridine under determined conditions and thereby interacts with the reagent in a molar ratio of 1 : 1. A photometric method for the determination of 0·05—2 μg of scandium/ml

by means of α-(2,4-dihydroxyphenylazo)-pyridine is worked out. Be, Mo, Ca and Mg do not interfere with the determination, but Zn, Co, Ni, Cd, Cu, Tl, In, Ga, Zr, Th, U and Fe do.

Zusammenfassung—Unter bestimmten Bedingungen gibt Scandium einen charakteristisch gefärbten 1:1 Kompex mit α-(2,4-dioxyphenylazo)-pyridin. Eine photometrische Methode wurde entwickelt zur Bestimmung von 0·05–2 μgSc/ml. Be, Mo, Ca, Mg stören nicht. Störung verursachen: Zn, Co, Ni, Cd, Tl, In, Ga, Th, Zr, U und Fe.

Résumé—L'ion scandium donne, dans certaines conditions, une coloration caractéristique avec l'α-(2,4-dihydroxyphénylazo)-pyridine par réaction dans le rapport molaire 1/1. Une méthode photométrique a été réalisée pour le dosage de 0,05–2 γSc/ml en utilisant ce réactif. Be, Mo, Ca, Mg ne gênent pas le dosage au contraire de Zn, Co, Ni, Cd, Cu, Tl, In, Ga, Zr, Th, U et Fe.

REFERENCES

[1] *Scandium*, Collection of articles IL., Moscow, 1958.
[2] R. Fresenius and G. Jander, *Handbuch der analyt. Chemie* Part 3, Vol. III. Springer Verlag, Berlin, 1942, p. 734.
[3] Collection of translated articles on the analytical chemistry of scandium. Gosgeoltekhizdat, Moscow, 1959.
[4] A. R. Eberle and M. W. Lerner, *Analyt. Chem.*, 1955, **27**, 1551.
[5] K. L. Cheng and T. R. Williams, *Chemist-Analyst*, 1955, **44**, 96.

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PHOTOMETRIC DETERMINATION OF MOLYBDENUM IN THE QUINQUEVALENT STATE BY MEANS OF 8-HYDROXYQUINOLINE-5-SULPHONIC ACID*

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Summary—A new photometric method has been worked out for the determination of small quantities of molybdenum (after its reduction to the quinquevalent state with hydrazine hydrochloride) using 8-hydroxyquinoline-5-sulphonic acid. From 3 to 20 mg of molybdenum can be determined by the method. Large quantities of tungsten, as well as magnesium, calcium, barium, nickel, cadmium, aluminium, thorium, bivalent manganese, tervalent chromium and small quantities of bismuth, copper and uranium do not interfere with the determination of molybdenum.

THE literature[1] contains references to the fact that the addition of 8-hydroxyquinoline-5-sulphonic acid to a solution of a salt of quinquevalent molybdenum followed by heating leads to the appearance of an intensely red coloration. In the cold, the reagent gives a soluble yellow compound with quinquevalent molybdenum, which is evidently not of great interest to analytical chemistry. Sexavalent molybdenum (at a concentration of 0·005 M/l.) is not precipitated by 8-hydroxyquinoline-5-sulphonic acid at a pH of 4–8† and does not form any coloured compounds with it. Most ions of other metals are thereby also not precipitated and do not form any soluble compounds having a characteristic colour.

The aim of this study was the clarification of the possibility of utilising 8-hydroxyquinoline-5-sulphonic acid for the photometric determination of molybdenum in the presence of other elements.

EXPERIMENTAL

Reagents

10^{-2}M solution of quinquevalent molybdenum: Two-five ml of a solution of hydrazine hydrochloride (concentration: 0·01 g/ml) and 1–3 ml of conc. hydrochloric acid are placed in a 100-ml beaker, and the volume is then made up to 20 ml with water. The solution is heated to boiling and 9·44 ml of a 0·05136*M* solution of sodium molybdate is added dropwise. Boiling is continued for a further few min, then the solution is transferred to a 50-ml calibrated flask, cooled and the volume made up to the mark with water.[2]

0·1M *solution of 8-hydroxyquinoline-5-sulphonic acid:* Prepared by dissolving 2·3 g of crystalline reagent‡ in 100 ml of water followed by the addition of a small amount of 1*M* sodium hydroxide solution. The suspension obtained is filtered, the solution is neutralised by the addition of hydrochloric acid until neutral or slightly acid to a universal indicator paper.[3]

The concentration of the aqueous solution of sodium molybdate is determined by the oxine method.[4]

Solution of the reducing agent: Twenty g of hydrazine hydrochloride is dissolved in a small amount of distilled water and the solution is neutralised with alkali until neutral to universal indicator paper. The volume is then made up to 100 ml with water.

Acetate buffer solution (pH 3·6*):* One hundred ml of 1*M* sodium acetate is mixed with 90 ml of 1*M* hydrochloric acid and the volume is made up to 250 ml with water.

* Translated from the Russian: *Vestnik. Mosk. Univ., Ser. II, Khim.* 1961, No. 2, 36.
† One product is precipitated at a pH of 2–3.
‡ 8-Hydroxyquinoline-5-sulphonic acid was synthesised by the usual method.[3]

Conditions for the formation of a compound between quinquevalent molybdenum and 8-hydroxyquinoline-5-sulphonic acid

Molybdenum^{V} forms two soluble complex compounds with 8-hydroxyquinoline-5-sulphonic acid. At room temperature a yellow compound is formed which slowly changes to a red one on prolonged standing. On heating an intensely red compound is formed almost immediately. The formation of two different compounds was established earlier on. Molybdenum^{V} does not give a precipitate with 8-hydroxyquinoline-5-sulphonic acid at pH values of 3–10. The explanation for this lies in the presence of the sulphonic-group in the reagent.

The red coloured compound of molybdenum^{V} with 8-hydroxyquinoline-5-sulphonic acid is very stable, which is confirmed by the fact that it does not undergo hydrolysis even in a strongly alkaline medium in the presence of an excess of 8-hydroxyquinoline-5-sulphonic acid; it should be noted that a solution of $(NH_4)_2MoOCl_5$ is readily hydrolysed.

Solutions of the red compound of molybdenum^{V} used to derive the absorption curve were prepared in the following manner: an excess (10 ml) of a 0·1*M* solution of 8-hydroxyquinoline-5-sulphonic acid was added to 20 ml of a hot solution containing 0·5 ml of a $10^{-2}M$ solution of molybdenum^{V}, the pH of the solution was adjusted to a value of 4·01 by means of a glass electrode and the mixture was heated on a boiling water bath for 20 min; the solution obtained was cooled, diluted to the mark with water in a 50-ml calibrated flask and the optical density was measured at different wavelengths on an SF-4 spectrophotometer, with reference to a blank solution prepared in an identical manner but without the addition of molybdenum (Fig. 1, curve 1). The absorption curve of a $10^{-2}M$ solution of 8-hydroxyquinoline-5-sulphonic acid at a pH of 4·77 is also shown in Fig. 1 (curve 2).

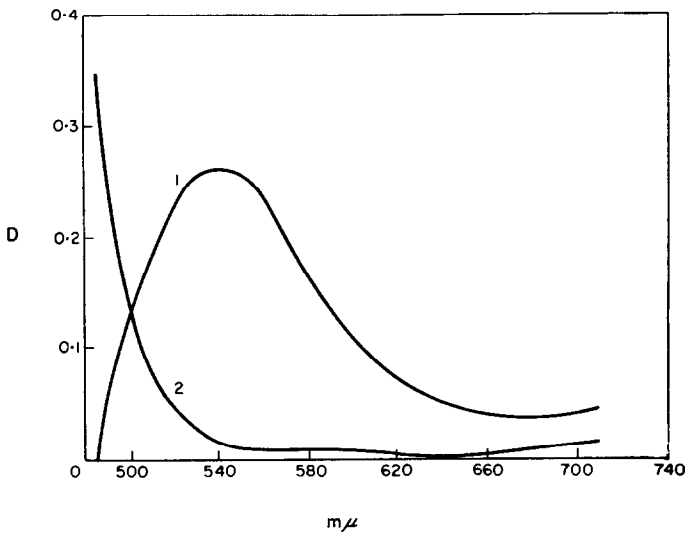


FIG. 1—Light absorption curves:
1-Compound formed between molybdenum^{V} and 8-hydroxyquinoline-5-sulphonic acid. Concentration in the final solution: $10^{-4}M$ of molybdenum^{V} and $10^{-2}M$ of 8-hydroxyquinoline-5-sulphonic acid; pH 4·01; after heating; optical density measured with respect to a $10^{-2}M$ solution of 8-hydroxyquinoline-5-sulphonic acid at pH 4·77;
2-$10^{-2}M$ solution of 8-hydroxyquinoline-5-sulphonic acid at pH 4·77. Optical density measured with respect to water.

The absorption curve of the red coloured compound formed between molybdenum^{V} and 8-hydroxyquinoline-5-sulphonic acid in the wavelength region of 480 mμ to 700 mμ exhibits only one maximum at 540 mμ. At 540 mμ the reagent absorbs practically no light.

The apparent molar absorption coefficient of molybdenum compound under the conditions of the spectrophotometric determination has a value of 5180.

The optimum pH value of the solution for the formation of the red compound between molybdenum^{V} and 8-hydroxyquinoline-5-sulphonic acid lies in the interval of 3–4·5 (Fig. 2). Since the

acetate ion does not interfere, the required medium may be produced by the addition of an acetate buffer solution.

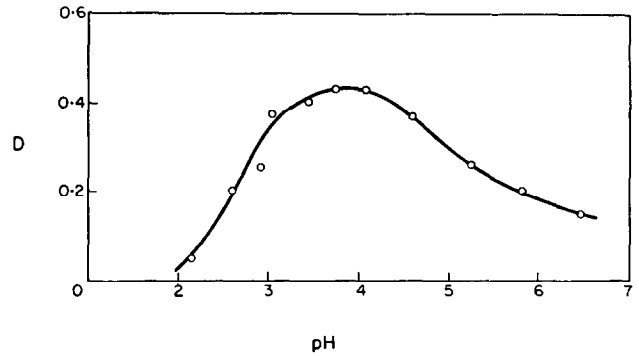


FIG. 2—Influence of pH on the magnitude of the optical density of solutions of the compound formed between molybdenum and 8-hydroxyquinoline-5-sulphonic acid.

The reduction of sexavalent molybdenum can be accomplished at a pH of 3–4·5 in the presence of large amounts of hydrazine hydrochloride if the solution contains 8-hydroxyquinoline-5-sulphonic acid which gives a very stable compound with molybdenum^{V} as a result of which the formation of molybdenum blue is not observed. Five ml of 0·1*M* neutral 8-hydroxyquinoline-5-sulphonic acid solution and 5 ml of acetate buffer solution having a pH of 3·1 are added to 15 ml of a solution containing 0·5 ml of a $10^{-2}M$ solution of sodium molybdate, and this is followed by the addition of 0·2, 1·0, 1·5 or 3·0 ml of a neutral or faintly acid solution of hydrazine hydrochloride (0·2 g/ml). The resultant solution is heated on a boiling water bath for a given time, cooled with water to room temperature, transferred to a 50-ml calibrated flask and the volume is made up to the mark. The optical density is then measured at 540 mμ with respect to water. The results are shown in Fig. 3.

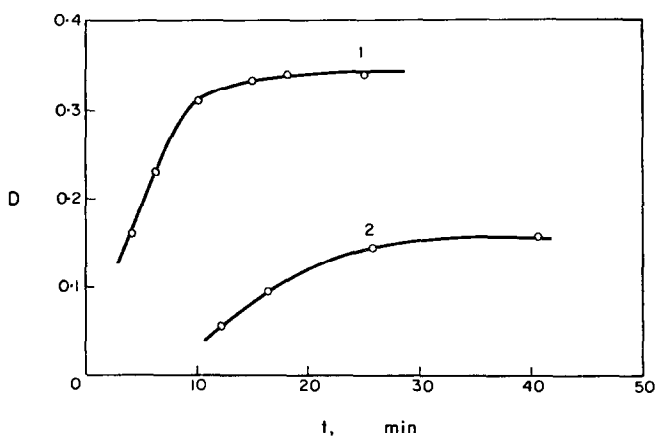


FIG. 3—Influence of the heating time on the optical density of the solution of the compound: 1- in the presence of 1·0 ml of a solution of 0·2 mg/ml of hydrazine hydrochloride in 25 ml final volume; 2- in the presence of 0·2 ml of a solution of 0·2 mg/ml of hydrazine hydrochloride in 25 ml final volume.

The optical densities of the solutions to which 1·0, 1·5 and 3·0 ml of a hydrazine hydrochloride solution containing 0·2 g/ml had been added, after which the solutions had been heated for 15 min, were practically identical (Fig. 3, curve 1). The formation of molybdenum blue was not observed at pH values of 3–4·5 or 6–7. Thus, in the photometric determination of molybdenum, molybdenum^{VI} may be reduced to molybdenum^{V} at a pH of 3·1, whereby the heating time on the boiling water bath amounts to 15–25 min and the necessary amount of hydrazine hydrochloride ($NH_2NH_2.2HCl$) is of

the order of 1–3 ml of a solution containing 0·2 g/ml to 25 ml of the solution to be analysed. At low concentrations of hydrazine hydrochloride (0·2 ml) the sensitivity of the reaction is lowered to a considerable extent (Fig. 3, curve 2), evidently as a result of the incomplete reduction of molybdenum[VI]. The optical density of the solutions obtained does not depend on the amount of hydrazine within the limits of 1–2·5 ml (heating time 20 min).

Without heating, the formation of the red molybdenum compound is also observed when a large amount of hydrazine is present and the intensity of the coloration increases with the time. But the colour has not attained its maximum value and constancy after a period of 3 hr.

For a complete development of the coloration more than 80 m mol of 8-hydroxyquinoline-5-sulphonic acid is required per m mol of molybdenum.[VI]

The intensity of the red colour of the solutions decreases slowly with time and after 24 hr the colour has disappeared. However, during the first 3 hr the optical density of the solutions remains practically constant.

Solutions of the compound of molybdenum[V] with 8-hydroxyquinoline-5-sulphonic acid obey Beer's law within the limits of 3–13 μg/ml of molybdenum. Ten ml of a weakly acid molybdate solution containing from 0·15–0·65 mg of molybdenum, and whose concentration has been determined accurately, are placed into a 50-ml beaker. Five ml of neutral 0·1*M* 8-hydroxyquinoline-5-sulphonic acid solution are added, followed by 1·5 ml of neutralised hydrazine hydrochloride solution containing 0·2 g/ml and 10 ml of acetate buffer (pH 3·6). The mixture is stirred and the beaker is covered with a watch glass; it is then placed on a boiling water bath and heated for 15–25 min. The

TABLE I.—DETERMINATION OF MOLYBDENUM IN THE PRESENCE OF TUNGSTEN AND OTHER FOREIGN IONS (0·38 MG OF MOLYBDENUM PRESENT)

Foreign ions, *mg*	Ratio of molybdenum to foreign ion	Molybdenum, *mg*	
		Found	Error
4·0 Ca	1:10	0·38	0
1·9 Mg	1:5	0·39	+0·01
54·8 Ba	1:140	0·34	−0·04
1·2 Ni	1:3	0·38	0
2·2 Cd	1:6	0·38	0
3·3 Mn	1:8	0·39	+0·01
7·0 Cu	1:18	0·41	+0·03
8·5 Cu	1:21	0·43	+0·05
1·0 Cr	1:2·5	0·38	0
3·1 Cr	1:8	0·37	−0·01
1·2 Al	1:3	0·38	0
4·2 Bi	1:11	0·35	−0·03
4·2 Bi	1:11	0·34	−0·04
1·0 Th	1:2·5	0·37	−0·01
0·24 U	1:0·6	0·37	−0·01
1·2 U	1:3	0·41	+0·03
32·5 KCN	1:80	0·37	−0·01
53·6 $Na_2C_2O_4$	1:134	0·38	0
60·0 $C_4H_6O_6$	1:150	0·26	−0·12
72·0 Complexone III	1:180	0·11	−0·27
1·0 V	1:2·5	0·71	+0·33
5·0 W	1:13	0·39	+0·01
10·0 W	1:25	0·35	−0·03
20·0 W	1:50	0·37	−0·01
30·0 W	1:75	0·34	−0·04
40·0 W	1:100	0·37	−0·01
30·0 W	1:75	0·39	+0·01
50·0 W	1:125	0·43	+0·05

molybdenum thereby passes quantitatively into the red form. The red solution obtained is cooled with cold water to room temperature, transferred to a 50-ml calibrated flask, and the beaker washed out thoroughly with distilled water. The volume is then made up to the mark with water, the contents of the flask are mixed and the optical density of the solution is determined at 540 mμ with respect to water, at least 2 hr after cooling.

Determination of molybdenum in the presence of tungsten and other elements

The photometric determination of molybdenum is carried out under the same conditions as those employed in verifying the applicability of Beer's law. Sexavalent tungsten does not form any coloured compounds with 8-hydroxyquinoline-5-sulphonic acid and therefore does not in any way influence the results of the molybdenum determination. However, in the presence of large amounts of tungsten (more than 10 mg) the amount of reagent added must be increased (two to three-fold). Vanadates give a red colour with the reagent, and iron^{II} a green colour. The last two elements interfere to a marked extent with the determination of molybdenum. Cobalt, zinc and larger amounts of copper give yellow or greenish-yellow coloured precipitates with the reagent on heating, and they also interfere with the determination. Complexone III and tartaric acid interfere with the determination as they form stable complexes with quinquevalent molybdenum.*

CONCLUSIONS

A new photometric method for determining small amounts of molybdenum by means of 8-hydroxyquinoline-5-sulphonic acid (after its reduction to the quinquevalent state by means of hydrazine hydrochloride) is developed. The method permits the determination of 3–20 mg/ml. Large amounts of tungsten, and also magnesium, calcium, barium, nickel, cadmium, aluminium, thorium, manganese^{II}, chromium^{III} and small amounts of bismuth, copper and uranium do not interfere with the molybdenum determination.

Zusammenfassung—Eine neue photometrische Methode wurde entwickelt, um kleine Mengen von Molybdän (nach Reduktion zur fünfwertigen Stufe) mit 8-Oxin-5-sulfonsäure zu bestimmen. 3–20 μg/ml können erfasst werden. Grosse Mengen von W, sowie Mg, Ca, Ba, Ni, Cd, Al, Th, Mn(II), Cr(III) und kleine Mengen von Bi, Cu und U stören nicht.

Résumé—Les auteurs ont mis au point une nouvelle méthode photométrique de dosage de faibles quantités de molybdène (après sa réduction à l'état pentavalent par le chlorure d'hydrazinium) à l'aide d'acide sulfo-5 oxy-8 quinoléine. Cette méthode permet de doser de 3 à 20 μg/ml de Mo. De grandes quantités de tungstène, ainsi que de magnésium, calcium, baryum, nickel, cadmium, aluminium, thorium, manganèse(II), chrome(III) et de faibles quantités de bismuth, cuivre et uranium ne gênent pas le dosage du molybdène.

REFERENCES

[1] A. I. Busev and Chang Fan, *Zhur. analit. Khim.*, 1960, **15**, 457.
[2] *Idem, ibid.*, 1959, **14**, 445.
[3] L. M. Kul'berg, *Sintezi organicheskikh reaktivov*. Goskhimizdat, Moscow, 1947, p. 79.
[4] R. G. Hollingshead, *Oxine and its derivatives*. Butterworths Sci. Publ., London, 1954, 2, part II, 430.

* Although the compound formed between molybdenum^{V} and 8-hydroxyquinoline-5-sulphonic acid is less stable than the compound formed with Complexone III, it is not suitable as a complexometric indicator for titrating quinquevalent molybdenum because of the unsharp colour change at the end-point (both at room temperature and on heating).

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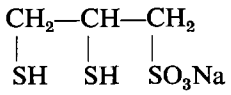
UNITHIOL AS A REAGENT FOR MOLYBDENUM*

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Summary—Unithiol (sodium 2,3-dimercaptopropanesulphonate) forms coloured complexes with molybdenum in acid solutions. The nature of these complexes is discussed, and it is concluded that Mo^{VI} is reduced to Mo^{V} by the reagent. Coloured complexes contain molybdenum^{V} and probably molybdenum^{VI}. Unithiol is a promising reagent for molybdenum. It has a high degree of selectivity. Cr and Hg^{II} do not give colours in acidic solution, Hg^{I} gives a greyish-brown precipitate, and Pb^{II} gives a yellow precipitate.

UNITHIOL (sodium 2,3-dimercaptopropanesulphonate)



is a white fine crystalline substance, readily soluble in water and sufficiently stable in solution. Its synthesis has been worked out.[1] Unithiol is used in medicine as an antidote against heavy metal poisoning. As far as can be judged from the first publication,[2] unithiol is also a valuable analytical reagent.

Unithiol is capable of forming stable complex compounds with a series of metals. The complex compounds of unithiol with some metals are in some cases more stable than the corresponding complexonates. This enables it to be employed for masking when carrying out complexometric determinations, in particular when titrating in an ammoniacal medium.

Quinque- and sexavalent molybdenum (the latter at acidities of pH 4 to 0·5*M* in hydrochloric acid) interact with unithiol in an acidic medium, giving yellow colorations. The colour appears rapidly when the reagent is present in a large excess. The maximum colour is developed on standing for some time. In a neutral or alkaline medium quinque- and sexavalent molybdenum do not form coloured compounds. The optimum optical density of the solutions for molybdate concentrations of $10^{-4}M$ and unithiol concentrations of $10^{-3}M$ is obtained at pH 1·5–2·7.

The absorption curves of the solutions obtained when mixing compounds of quinque- and sexavalent molybdenum with unithiol are shown in Fig. 1. All of the solutions were prepared in the following manner:

The necessary amount of sexa- and quinquevalent molybdenum salt (final molybdenum concentration $10^{-4}M$) was placed in a 25-ml calibrated flask, then hydrochloric acid was added until the desired pH had been attained. A ten-fold molar amount of the reagent was added and the solution made up to the volume with water. The optical densities of the solutions were determined with respect to water, after 1·5 hr in the case of compounds of molybdenum^{V} and after 12 hr in the case of compounds of molybdenum^{VI}. Solutions of the reagent alone absorbed practically no light in the region of long wavelengths at which the solutions of molybdenum compounds absorb.

The absorption curve (Fig. 1, curve 1) of solutions of compounds of molybdenum^{V} exhibits a maximum at 335 mμ. Absorption curves of solutions obtained by mixing

* Translated from the Russian: *Zhur. Vsesoyuz. Khim. Obschestva im. D. I. Mendeleeva*, 1961, **6**, 237.

molybdate with unithiol, also exhibit a maximum at 335 mμ (Fig. 1, curve 2). When using a hundred-fold molar amount of unithiol the absorption maximum undergoes practically no change. All of these curves have roughly the same region of maximum absorption and, consequently, characterise absorption of the same molybdenum compound.

The coincidence of the absorption curves of compounds of quinquevalent molybdenum with those of compounds obtained starting from sexavalent molybdenum

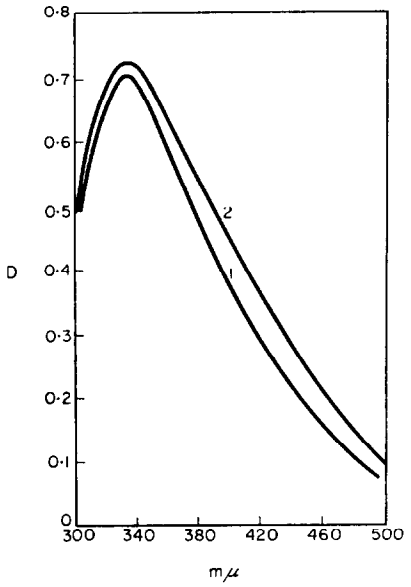


FIG. 1—Absorption curves of solutions of molybdenum^{VI} and molybdenum^{V} with unithiol: 1—Molybdenum^{V} at pH 2; 2—Molybdenum^{VI} at pH 1·52. Concentration of molybdenum^{VI} and molybdenum^{V} $1{\cdot}03 \times 10^{-4}M$, concentration of unithiol $10^{-3}M$.

leads to the conclusion that molybdenum^{VI} is reduced by unithiol to the quinquevalent state and that the compounds of molybdenum^{V} are stable. However, there also undoubtedly exists a compound of molybdenum^{VI} with unithiol.

The apparent molar absorption coefficient of solutions of compounds of quinquevalent molybdenum at 335 mμ is equal to 7000 (pH 2). The optical density was measured after 1·5 hr. The apparent molar absorption coefficient of solutions obtained by mixing molybdate and unithiol was found to be equal to 7200 at 335 mμ (pH 1·5, 2 and 2·3). The optical density was measured after 12–15 hr.

The molar ratio in the interaction of molybdenum^{V} or molybdenum^{VI} was established by the method of isomolar series. Different volumes of a $0{\cdot}00943M$ solution of sodium molybdate or a salt of quinquevalent molybdenum were mixed with an $0{\cdot}00943M$ neutral unithiol solution in such a way that the sum of the molar concentrations of the two components in the final solution was always constant and equal to $7{\cdot}55 \times 10^{-4}M$. The concentration of the unithiol solution was determined by iodometric titration. The acidity was adjusted to pH 2 by the careful addition of a calculated amount of hydrochloric acid. After dilution to the mark with water the pH was checked by means of a glass electrode. The solutions were left to stand for

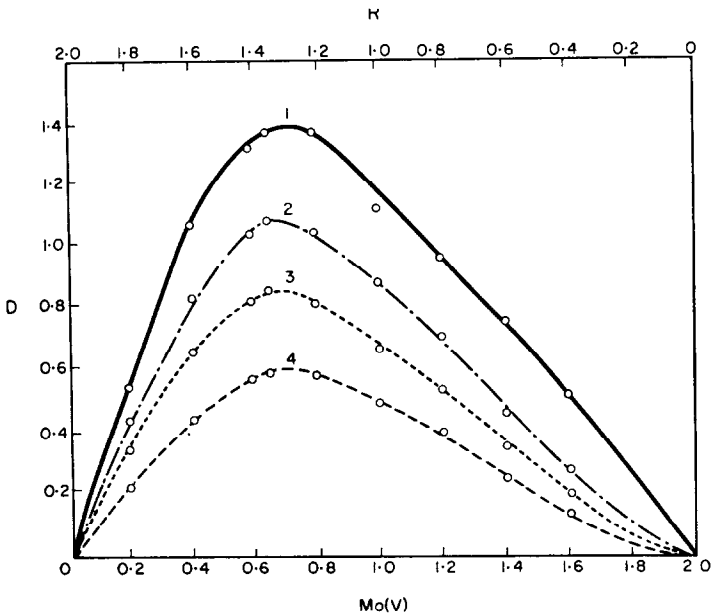


FIG. 2—Molar ratios in the interaction of unithiol with molybdenum^{V} (pH 2):
1—335 mμ; 2—370 mμ; 3—430 mμ.
The optical density was determined 3 hr after preparation of the solutions, with reference to water.

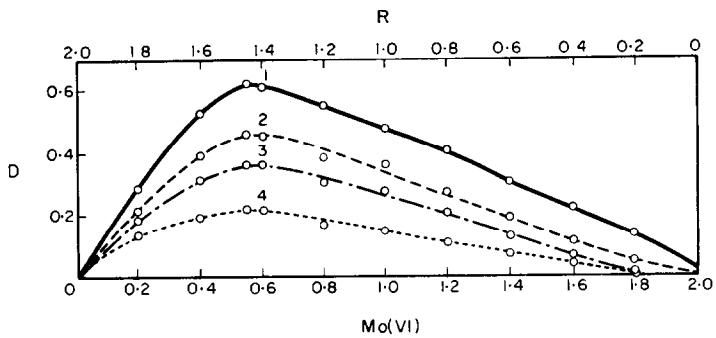
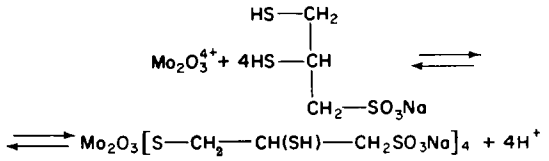


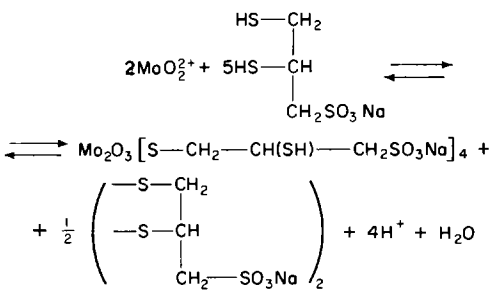
FIG. 3—Molar ratios in the interaction of unithiol with molybdenum^{VI} (pH 2):
1—335 mμ; 2—370 mμ; 3—390 mμ; 4—430 mμ.
The optical density was measured 24 hr after preparation of the solutions, with reference to water.

3 hr in the case of molybdenum^{V} (Fig. 2) or 24 hr in the case of molybdenum^{VI} (Fig. 3). The optical density was measured at 335, 370, 390 and 430 mμ.

Fig. 2 shows that the maximum of the optical density for solutions of the compound of quinquevalent molybdenum and unithiol occurs at a molar ratio of 1:2. On the basis of this, the following equation can be written for the reaction:



The maximum optical density for molybdenum^{VI} at pH 2, occurs at molar ratios of molybdenum to unithiol equal to 2:5 (Fig. 3). This confirms our conclusion that molybdenum^{VI} is reduced to molybdenum^{V} which also forms a coloured compound with unithiol. Evidently, 2 moles of molybdenum^{VI} are reduced by 1 mole of unithiol to the quinquevalent state and following this 4 moles of unithiol interact with 2 moles of molybdenum^{V}:



The reduction of sexavalent molybdenum to the quinquevalent state by unithiol was also confirmed by titration with iodine of a mixture of molybdate and unithiol solutions at pH 2. Three solutions containing known amounts of sodium molybdate and an excess of unithiol were prepared in 25-ml flasks. The solutions were prepared in the usual manner and on the next day they were titrated against a 0·01*M* solution of iodine in the presence of starch. At pH 2, quinquevalent molybdenum is not oxidised by iodine. A gradual weakening of the yellow colour is observed during the titration and close to the end-point the solution is completely colourless. The end-point of the titration is marked by the sharp transition to blue on addition of 1 drop of iodine, which does not disappear for several min. From the amount of iodine required to complete the titration the amount of unreacted unithiol is calculated, and the difference gives the amount of unithiol used in reducing molybdenum^{VI}. Unithiol bound to molybdenum is not oxidised by iodine. Thus, it was established that the reduction of 2 moles of sexavalent molybdenum requires 1 mole of unithiol. The results of the iodometric titration confirm the above proposed scheme for the interaction of unithiol with sexavalent molybdenum.

Unithiol as a reagent for molybdenum has a high degree of selectivity. Chromium and mercury^{II} do not give a coloration with unithiol in an acidic medium, mercury^{I} gives a greyish-brown precipitate at pH 2 and lead^{II} gives a yellow precipitate.

Thus, unithiol is undoubtedly a very promising reagent for molybdenum.

Zusammenfassung—Unitiol (Natrium-2,3-dimercaptopropansulfonat) bildet in saurem Medium farbige Komplexe mit Mo (V) and Mo (VI). Aus experimentellen Studien wurde geschlossen, dass Mo (VI) durch das Reagens zu Mo (V) reduziert wird. Unitiol is ein vielversprechendes Reagens für Molybdän und zeigt einen hohen Grad von Selektivität. Chrom und Hg (II) geben keine Färbung in saurer Lösung, Hg (I) gibt einen graubraunen, Pb (II) einen gelben Niederschlag.

Résumé—L'unithiol (2,3-dimercapto-propane sulfonate de sodium) forme des complexes colorés avec Mo (V) et Mo (VI) en solution acide. Las auteurs discutent la nature de ces complexes et concluent que Mo (VI) est réduit en Mo (V) par ce réactif. L'unithol est un réactif intéres sant pour le molybdène; il est très sélectif. Le chrome et le mercure (II) ne donnent pas de couleurs en solution acide, le mercure (I) donne un précipité brun grisâtre, et le plomb (II) donne un précipité jaune.

REFERENCES

[1] V. E. Petrun'kin, *Ukrain. khim. Zhur.*, 1956, **22**, 603.
[2] L. A. Vol'f, and J. E. Matuskov *Zavodskaya lab.*, 1959, **25**, 1438.

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IMPROVED ELECTRODES FOR THE CONTINUOUS MEASUREMENT OF SODIUM AND POTASSIUM

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Summary—A method for constructing sodium and potassium selective glass electrodes is described. The electrodes are capable of continuous, accurate, and reproducible recording of $\Delta(Na^+)$ and $\Delta(K^+)$. The pair of electrodes is able to discriminate a change of less than 0·5 mequiv/l. of sodium and 0·5 mequiv/l. of potassium when used in mixed sodium and potassium solutions in the biological range of 130–150 mequiv/l. of sodium and 2–6 mequiv/l. of potassium. When used for continuous measurements a simple circuit reduces the "sodium error" inherent in the potassium electrode to less than 0·25 mequiv/l. of potassium with changes in sodium from 130 to 150 mequiv./l.

INTRODUCTION

UNTIL the recent development of sodium and potassium sensitive glass electrodes, no reliable reproducible method for continuous measurement of these cations in blood and tissues was available. Previous methods necessitated repetitious sampling of the specimen with obvious disadvantages. Eisenman, Rudin and Casby,[1] elaborating on the previous work of Horovitz[2] and Lengyel and Blum,[3] developed a sodium sensitive glass designated NAS_{11-18}.*

They also defined the cation selectivity of an electrode glass in terms of the parameter k_{AB} of a new empirical equation:

$$E = E^\circ + \frac{RT}{F} \ln \left[(A^+)^{1/n_{AB}} + k_{AB}^{1/n_{AB}} (B^+)^{1/n_{AB}} \right]^{n_{AB}}.\dagger$$

The original NAS_{11-18} sodium selective electrode glass described by Eisenman, Rudin and Casby had a sodium selectivity with regard to potassium of 250 to 1 at pH 7·6 ($k_{NaK} = 4 \times 10^{-3}$). Electrodes constructed from this glass had limited practical value because no insulating glass had been found to which the sensitive glass could be sealed. Friedman and associates[4,5] constructed a capillary type of

* The designation NAS_{11-18} describes the final composition of the glass as determined by analysis, namely: Na_2O, 11 moles%; Al_2O_3, 18 moles%; SiO_2, 71 moles%. The NAS_{11-18} glass we utilised was obtained from Corning Glass Works and was prepared to approximate the original composition.

† E = measured e.m.f.; E° = standard potential; R = ideal gas equation constant; T = temperature (absolute); F = Faraday constant; (A^+) and (B^+) = activity of ionic species A^+ and B^+; n_{AB} and k_{AB} = empirical constants for a given glass composition and ionic pair A^+ and B^+. For the cation pair sodium and potassium (above pH 6), this equation simplifies at 22° to $E = E^\circ + 58 \log [(Na^+) + k_{NaK}(K^+)]$, since $n_{NaK} = 1$ for both glasses described.

For the described glasses, above pH 6, a value of $k_{NaK} = 0{\cdot}01$ indicates that 0·01 mole (Na^+) is equivalent to 1·0 mole (K^+) in determining electrode potential. A value of $k_{NaK} = 10$ indicates that 0·1 mole (K^+) is equivalent to 1·0 mole (Na^+) in determining electrode potential. The value k_{NaK} can be determined by measuring the potentials (E) of two solutions, one containing pure Na^+ of known activity and the other pure K^+ of known activity. The values for E at a known (Na^+) and zero (K^+), and at a known (K^+) and zero (Na^+) are thus determined and the two equations obtained are solved simultaneously for k_{NaK}.

sodium sensitive electrode by silvering the external surface of a capillary made of NAS_{11-18} glass, thus making a glass-to-silver electrode. This electrode had a 48 mV slope rather than the theoretical 58 mV slope for ten-fold dilutions of sodium activity at 22°. Using a special microforge, Hinke[6,7] was able to seal NAS_{11-18} to a high resistant insulating glass to produce microelectrodes. In this communication we describe a new method for constructing all glass sodium sensitive electrodes using NAS_{11-18}.

Potassium selective glass electrodes have been constructed from a new glass, KAS_{20-5}, developed in co-operation with Eisenman. This glass, KAS_{20-5}, has an initial or pre-melt composition of K_2O, 20 moles %; Al_2O_3, 5 moles %; and SiO_2, 75 moles %.* It has a potassium selectivity with regard to sodium of 10 to 1 (k_{NaK} = 10) which is close to the theoretical limit for glasses of the ternary systems: alkali metal oxide, Al_2O_3, SiO_2.[8,9] This glass is superior in selectivity and physical properties to potassium selective glasses composed of Na_2O, Al_2O_3 and SiO_2, made available to us by Eisenman. These NAS-type potassium selective glasses have only a 3–5 to 1 selectivity factor and relatively low softening point, about 500° as compared to 800° for KAS_{20-5}.

EXPERIMENTAL

Construction of the electrodes

Both sodium and potassium selective glass electrodes can be made utilising the following newly devised compression seal technique.† To make a probe type of electrode (Fig. 1), the sodium (NAS_{11-18}) or potassium (KAS_{20-5}) selective glass is drawn into a capillary having a diameter of approximately 1 mm and a wall thickness of approximately 0·1 mm. One end of the capillary is sealed and the glass capillary is then cut 8–10 mm from the closed end. The open end of the capillary is then inserted into the open end of a 5-mm diameter tube of a suitable insulating glass such as modified Fischer thermometer glass, a lead-containing glass having a softening point around 600–650°. By slowly rotating the end of this insulating glass in a gas–oxygen flame, the end is brought to working temperature and allowed to flow about the NAS_{11-18} or KAS_{20-5} glass. On cooling, a compression seal is formed between the two glasses.

Formation of the capillary electrode is very similar except that a capillary of NAS_{11-18} or KAS_{20-5} glass is placed through the centre of the cross bar of the T-shaped supporting tube made of the suitable insulating glass. A compression seal is then formed at each end of this T-piece as illustrated in Fig. 1. After some experience these electrodes can be made without significant breakage.

The glass electrode is completed by filling the insulating glass stem with 0·1*N* sodium chloride or or 0·1*N* potassium chloride solution, respectively, for the sodium selective and potassium selective electrodes. It is usually preferable to buffer the solution to an alkaline pH. Tris-hydroxymethyl-aminomethane is a convenient buffer. We have found it advantageous to layer a column of mineral oil or silicone fluid‡ above the filling solution. These are both good insulators (especially the latter) and also tend to reduce spurious electrical discharges by eliminating the fluid layer present on the inside surface of the insulating glass. A chlorided silver wire attached to a flexible shielded cable is used to complete the electrode.

Function of the electrode

Electrodes constructed from the NAS_{11-18} and KAS_{20-5} glasses gave theoretical slopes for ten-fold dilutions of the respective sodium or potassium ion activity as tested with varying dilutions of pure sodium chloride and potassium chloride solutions (above pH 6·0) using both a calomel reference

* Both NAS_{11-18} and KAS_{20-5} may be obtained from Dr. Martin E. Nordberg, Research and Development Division, Corning Glass Works, Corning, New York, U.S.A., as Corning Code #172 AVN and #X172 BHI, respectively.

† The glass electrode shells used in this study were constructed by Mr. Walter Angst, 18639 Blue Island Court, Roseville, Michigan, U.S.A., who devised the compression seal technique.

‡ Dow Corning 200 Silicone Fluid (#350), Dow Corning, Midland, Michigan, U.S.A.

electrode with liquid junction* and a Ag-AgCl electrode without liquid junction.† Though Eisenman, *et al.*[1] report a selectivity of 250 to 1 for electrodes constructed from their original NAS_{11-18} glass, the glass which we utilised had about one-half this selectivity (100 to 1).‡ As mentioned before, the potassium selective glass, KAS_{20-5}, has a 10 to 1 potassium to sodium selectivity as determined in pure sodium chloride and potassium chloride solutions.

Compensating the potassium electrode

It was deemed advisable to have the potassium electrode indicate only changes in potassium and not the combination of potassium and sodium as dictated by a selectivity factor (k_{Nak}) of only 10. Without some form of compensation the potassium electrode would respond to a change in sodium

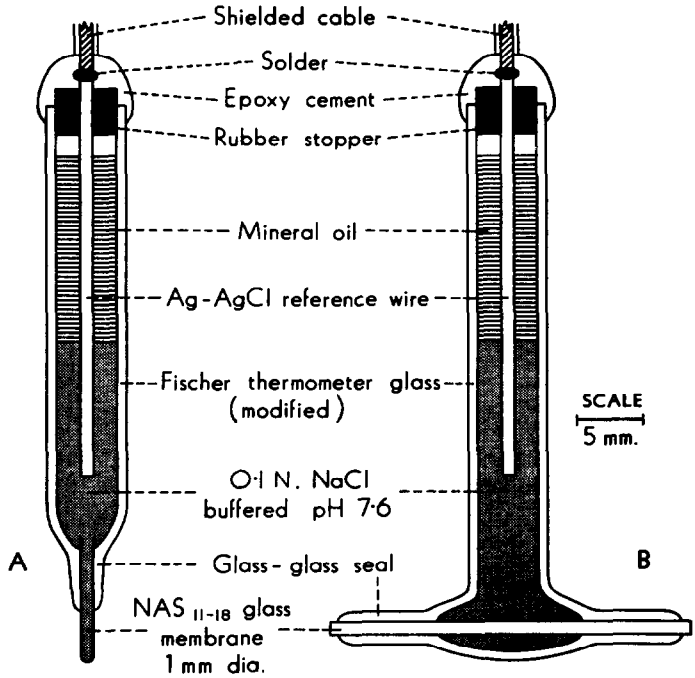


Fig. 1—Details of construction of the probe (A) and capillary (B) sodium sensitive glass electrodes. Similar potassium selective glass electrodes may be constructed by utilising KAS_{20-5} glass as the glass membrane and 0·1*N* potassium chloride for the filling solution.

from 130 to 150 mequiv/l. by an alteration in potential equivalent to about 1·5 mequiv/l. of potassium. A simple electronic circuit effectively reduces this "sodium error" when utilised in the biological range of sodium and potassium.

The output of each of the electrodes was amplified by a Radiometer PHM22 pH meter coupled to a Grass Model 5 Polygraph by a calibrated coupling unit. The circuitry of the coupling unit was modified as illustrated in Fig. 2. By placing the output of the sodium and potassium selective electrodes in opposition, the former output being modified by a voltage divider, A, the effect of sodium change on the potassium selective electrode can be minimised. If the voltage divider, A, is

* When using these electrodes with a liquid junction reference electrode in solutions of greater concentration than 0·2*N* sodium chloride, the values obtained for (Na^+) are progressively higher than those obtained by calculation utilising mean activity coefficients. No such discrepancy occurs when using a Ag-AgCl reference electrode without liquid junction or in measuring (K^+) regardless of reference electrode used. Hinke[7] has found a similar deviation at high concentrations of (Na^+).

† The mean activity coefficients for the calculation of sodium chloride and potassium chloride activity were obtained from tables in H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, 3rd Edition. Reinhold Publishing Co., New York, 1958.

‡ See footnote on page 1.

properly adjusted, calculations based on the formula of Eisenman, *et al** reveal that, for changes in sodium concentration from 130 to 150 mequiv/l. and potassium in the range of 2–6 mequiv/l., there is a potassium error of less than 0·25 mequiv/l. at the extremes of sodium and potassium concentration.

Testing the electrodes

In order to test the electrodes in continuously changing solutions of varying sodium and potassium concentration, a test apparatus was designed which almost completely eliminated artifacts caused by variations in flow and which was simple and easy to use. The particulars of this apparatus are described more fully elsewhere[10] but are schematically represented in Fig. 2. The electrodes were

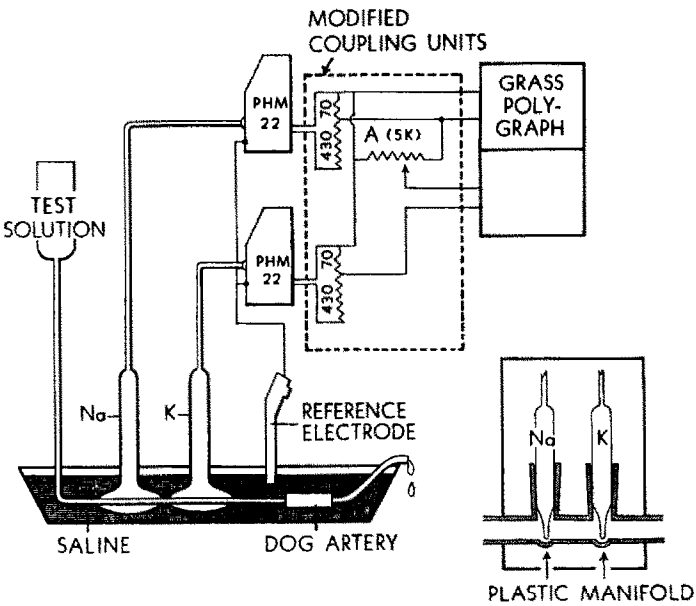


Fig. 2—Apparatus for testing the sodium and potassium selective electrodes. Note the diagram of the modified coupling units for use with Radiometer PHM22 pH meters and Grass model 5 Polygraph with low level d.c. pre-amplifiers. Voltage divider A is adjusted as described in the text to minimise "sodium error" of the potassium electrode. The plastic manifold used for testing the probe electrodes is illustrated in the insert.

placed in series such that the test solutions ran first through the sodium electrode, then through the potassium electrode. (A second potassium electrode was used so as to be able to compare changes in potential from a potassium electrode with and without electronic compensation.) Solutions were changed by pouring the new solution into the test solution flask when the flask contained no more than a few ml of old solution. Under these circumstances the solutions could not be instantaneously changed and there was always a little admixture of old and new solution.

The voltage divider "A" (Fig. 2) was adjusted so that there was a minimal variation in recorded potential from the potassium selective electrode when solutions of 130 and 150 mequiv/l. of sodium

* The assumption is made that the sodium electrode measures solely sodium ion activity. With a selectivity factor (k_{NaK}) of 1×10^{-3} or less, this assumption should be valid for sodium and potassium concentrations in the biological range. The potential changes derived from the sodium (ΔE_s) and potassium (ΔE_p) electrodes on change from 130 to 150 mequiv/l. sodium with a constant potassium concentration in the range of 2–6 mequiv/l. are:

$$\Delta E_s = E^\circ_s + 58 \log (Na_{150}^+) - [E^\circ_s + 58 \log (Na_{130}^+)]$$
$$\Delta E_p = E_p^\circ + 58 \log [(Na_{150}^+) + 10\, K^+_{2-6})] - (E_p^\circ + 58 \log [(Na_{130}^+) + 10(K^+_{2-6})]).$$

Since E_s is the larger of the two potential changes, it must be reduced by a factor, A, in order for the net change of potential for the electrodes placed in opposition to be zero ($A\,\Delta E_s - \Delta E_p = 0$). In the circuit, this alteration in E_s is accomplished by the voltage divider, A. Calculations based on these formulae were made assuming activity coefficients for sodium and potassium of 0·76 and 0·92, respectively.

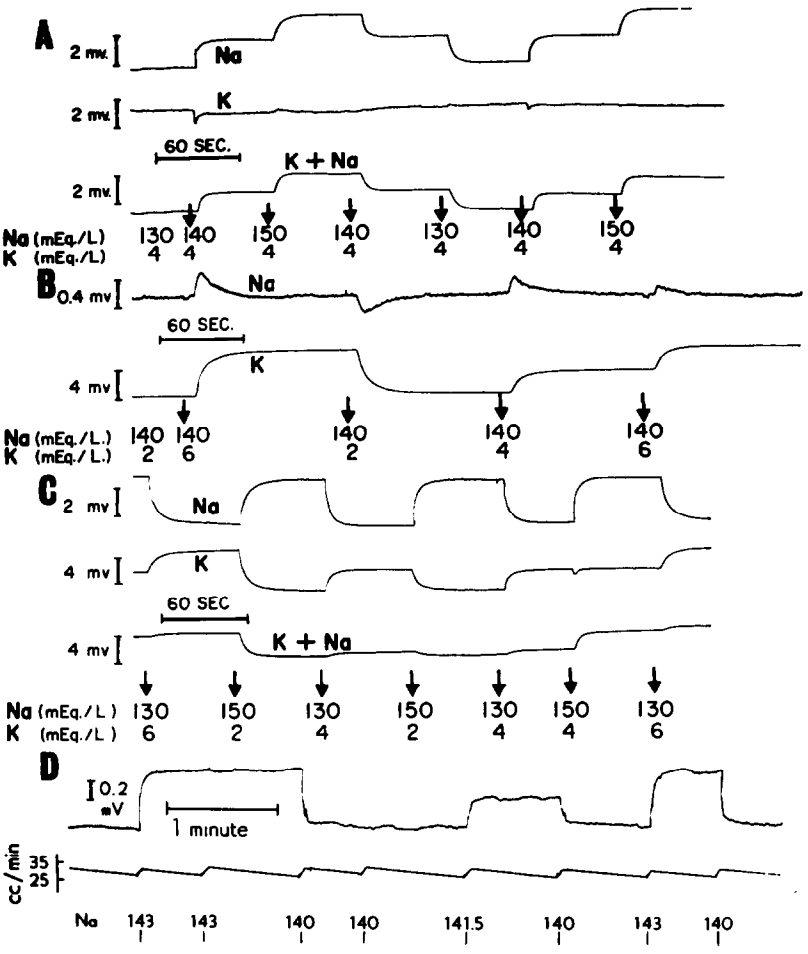


Fig. 3

A: Na, sodium electrode; K, compensated potassium electrode; K + Na, uncompensated potassium electrode. With voltage divider A (Fig. 2) adjusted, as directed in the text, change in sodium concentration from 130–150 mequiv/l. produces less than 0·2 mequiv/l. error in potassium. The transient positive and negative waves following the addition of a new solution are caused by (1) the unequal initial response time to changes in sodium of the sodium and potassium electrodes in opposition, and (2), in this study, the new solution coming into contact first with the sodium and then the potassium electrode. The sodium and uncompensated potassium electrode show similar potential changes. The delay between the pouring in of a new solution into the flask and the initial response of the electrodes is primarily determined by the time required for the new solution to traverse the rubber tubing.

B: Except for the transient positive and negative waves (see text), the sodium electrode shows almost no change when potassium is varied between 2 and 6 mequiv/l. The potassium electrode responds faithfully to the change in potassium.

C: Comparison with the response of compensated and uncompensated potassium electrodes to changes in both sodium and potassium. When recording from the uncompensated potassium electrode, a decrease in potassium tends to be nullified by a simultaneous increase in sodium, and *vice versa*.

D: Na in mequiv/l. Small changes in sodium concentration are readily detected and recorded by the sodium selective electrode. Changes in rate of flow (lower trace) at a constant sodium concentration do not significantly alter potential.

chloride each containing 4 mequiv/l. of potassium chloride, were alternatively flowed through the electrodes. Following this procedure, the effect of varying the sodium concentration in the presence of a constant potassium concentration was tested. As illustrated in Fig. 3A, variations in sodium concentration from 130 to 150 mequiv/l. of sodium at a constant potassium concentration of 4 mequiv/l. produced an error in the voltage recorded from the KAS_{20-5} electrode corresponding to about 0·2 mequiv/l. potassium. By comparison, the potential variation recorded from the potassium selective electrode of Friedman *et al.*[11] (not compensated) was approximately equivalent to 4 mequiv/l. potassium for a similar change in sodium.

A similar test of the selectivity of the sodium electrode was likewise carried out by varying the potassium concentration through the biological range and keeping the sodium concentration constant at 140 mequiv/l. (Fig. 3B). Except for a transient change in potential which lasts less than 1 min, the potential derived from the sodium electrode remains practically unchanged (verifying the assumption upon which the electronic compensation of the potassium electrode is based). The transient increase and decrease in potential seen when the potassium concentration increased or decreased, respectively, was also noted by Friedman *et al.*[11] and appears to be a function of the sodium electrode.

The ability of the electrodes to discern small changes in concentration is good as can be seen from Fig. 3 (A, B, D) in which changes in sodium and potassium in the biological range are easily discernable. In Fig. 3D it should also be noted that changes in the rate of flow (lower trace) without changes in sodium concentration do not significantly alter the recorded potential.[10]

The probe electrodes were tested in a similar continuous flow system using the plastic manifold illustrated in Fig. 2 (insert). The results from the probe electrodes were essentially identical with those from the capillary electrodes.

Acknowledgements—The authors wish to thank Dr. George Eisenman for his many helpful suggestions during the course of this study. The work was aided by a grant from the Kresge Foundation.

Zusammenfassung—Eine Methode zur Konstruktion von Na- und K-empfindlichen Glaselektroden wird beschrieben. Die Elektroden sind imstande $\Delta(Na^+)$ und $\Delta(K^+)$ kontinuierlich, genau und reproduzierbar anzuzeigen. Das Elektrodenpaar ist imstande eine Änderung von weniger als 0·5 mVal/Liter Na^+ und K^+ anzuzeigen, wenn in Na-K-Lösungen im biologischen Bereich von 130–150 mVal/L Na und 2–6 mVal/L K gearbeitet wird. Wenn zu kontinuierlichen Anzeigen verwendet, ist es möglich durch einen einfachen Stromkreis den "Natriumfehler" der K-Elektrode auf weniger als 0·25 mVal/L herabzudrücken.

Résumé—Les auteurs décrivent une méthode de fabrication d'électrodes de verre sélectives pour Na et K. Les électrodes sont capables de donner des valeurs continues, précises et reproductibles de $\Delta(Na^+)$ et $\Delta(K^+)$. La paire d'électrodes est susceptible de mettre en évidence une variation de moins de 0,5 meq./l. de Na et 0,5 meq./l. de K, quand elle est utilisée dans des mélanges de solutions de Na et de K dans le domaine biologique de 130–150 meq./l. de Na et 2–6 meq./l. de K. Pour des mesures continues, un simple circuit réduit "l'erreur de sodium" inhérente à l'électrode de K à moins de 0,25 meq./l. de K pour des variations de Na de 130 à 150 meq./l.

REFERENCES

[1] G. Eisenman, D. O. Rudin and J. U. Casby, *Science*, 1957, **126**, 831.
[2] K. Horovitz, as reviewed by M. Dole, *The Glass Electrode*. J. Wiley and Sons, Inc., New York, 1941, p. 28.
[3] B. Lengyel and E. Blum, *Trans. Faraday Soc.*, 1934, **30**, 461.
[4] S. M. Friedman, J. D. Jamieson, J. A. M. Hinke and C. L. Friedman, *Proc. Soc. Exp. Biol. Med.*, 1958, **99**, 727.
[5] S. M. Friedman, J. D. Jamieson and C. L. Friedman, *Amer. J. Physiol.*, 1959, **196** 1049.
[6] J. A. M. Hinke, *Nature*, 1959, **184**, 1257.
[7] *Idem.*, *J. Physiol.*, 1961, **156**, 314.
[8] G. Eisenman, *On the Elementary Atomic Origin of Equilibrium Ionic Specificity*. Presented in the discussion at the Symposium on *Membrane Transport and Metabolism* of the Czechoslovak Academy of Science, Prague, 1960.
[9] G. Eisenman, personal communication.
[10] H. D. Portnoy, L. M. Thomas and E. S. Gurdjian, *J. Appl. Physiol.*, in press.
[11] S. M. Friedman, J. D. Jamieson, M. Nakashima and C. L. Friedman, *Science*, 1959, **130**, 1252

Talanta, 1962, Vol. 9, pp. 125 to 132. Pergamon Press Ltd. Printed in Northern Ireland

SPECTROPHOTOMETRIC STUDIES ON TECHNETIUM AND RHENIUM

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Summary—The behaviour of technetium and rhenium with three reagents, potassium ferrocyanide, sulphosalicylic acid, and α-picolinic acid is discussed. With the first reagent, technetium and rhenium in the presence of bismuth amalgam or stannous chloride, form coloured solutions which show maximum absorption at widely different wavelengths, thus permitting the spectrophotometric determination of both elements in the presence of one another. As little as 2 μg of technetium can be determined by this method.

Sulphosalicylic acid with pertechnetate which has been reduced with stannous chloride produces an orange-red coloration suitable for the determination of the element. The method has the advantage that the element can be determined in the presence of fairly large amounts of rhenium, manganese and molybdenum.

When pertechnetate is reduced with ascorbic acid, α-picolinic acid yields a yellow-red solution which provides a sensitive method for the spectrophotometric determination of the element.

The types of complex formed with the reagents are discussed.

ALTHOUGH the element technetium was first obtained[1] in 1937 by neutron bombardment of a molybdenum target, until recently the amount available has been very small. This has resulted in a lack of information on the general and analytical chemistry of the element.[2] With the availability of higher neutron fluxes for bombardment purposes and the development of a method for the isolation of milligram quantities of the element from irradiated uranium and fission-product waste solutions,[3] there has been an increase in the supply of technetium and a number of papers on its analytical behaviour[4,5,6] have appeared.

In 1959 Jasim, Magee and Wilson,[7] after an ultramicro qualitative investigation, reported several new reagents for the detection of technetium and, the following year, Foreman *et al.* carried the investigation of some of these and other reagents a stage further.[3] The latter authors found that while many of the reagents showed possibilities there were often associated disadvantages. Ammonium thiocyanate[5] gave a reaction similar to iron; dimethylglyoxime[7] was too insensitive; thioglycollic acid and diphenylcarbazide also form coloured complexes with rhenium. In none of the cases outlined, except ammonium thiocyanate, have absorption spectra been determined, nor have colorimetric methods been developed.

In the work in this department the expanding field of research with technetium and rhenium necessitated an accurate method for the determination of these two elements, with a knowledge of the influence of associated elements such as molybdenum, ruthenium and manganese. Investigations were therefore begun to discover reagents which would provide simple, direct and sensitive methods for the colorimetric determination of both elements. The results of the spectrophotometric investigations carried out in this connection are reported in this paper.

NEW REAGENTS FOR TECHNETIUM

1. *Potassium Ferrocyanide*

When acted on by strong reducing agents such as stannous chloride, potassium ferrocyanide in the presence of hydrochloric acid produces a brownish yellow complex with the lower valent states of technetium. This coloured complex can be extracted into amyl alcohol from acid solution. If stannous chloride is replaced by bismuth amalgam, or mercury, or concentrated hyrdochloric acid, a distinctive blue colour is obtained which may also be extracted into amyl alcohol. With hydrobromic acid in place of hydrochloric acid, formation of the technetium blue occurs more slowly. With sulphuric acid a transient blue colour turns to reddish-violet and, after some time, a dark violet compound is precipitated. This reagent may be used as a quantitative test for the presence of technetium.

Detection of technetium

Procedure: Place in the cavity of a spot plate, 1 drop of the test solution and 1 drop of a freshly prepared 5% solution of potassium ferrocyanide. (If iron is present an immediate blue colour is obtained). To the solution now add 1 or 2 drops of concentrated hydrochloric acid. In the presence of technetium the characteristic blue colour slowly begins to develop. To confirm the presence of this element, add to the solution 1 drop of 10% stannous chloride in 6*M* hydrochloric acid. The blue colour of technetium is immediately changed to colourless or slightly brownish-yellow, depending on the concentration of technetium. If to this solution 1 drop of 10% hydrogen peroxide is now added, the blue colour reappears but will pass right through to colourless with excess of the peroxide.

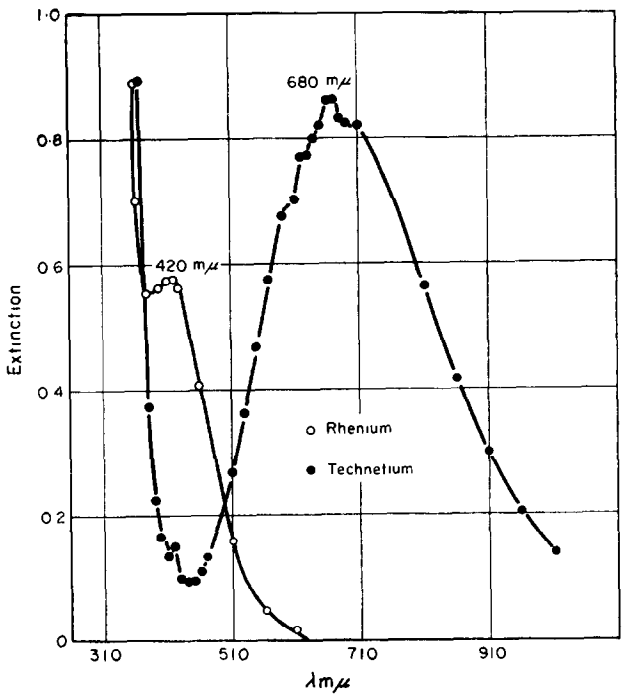


FIG. 1.—Absorption spectra of ferrocyanide complexes.

Metals which form colours or precipitates with ferrocyanide tend to obscure this test. It is, therefore, advisable to separate technetium (as pertechnetate) from these metals by a cation-exchange technique, before applying the test.

Molybdate, under similar conditions, forms a reddish-brown colour or produces a colloidal precipitate.[8] Perrhenate does not interfere unless stannous chloride[9] or bismuth amalgam is used, when red and brownish-yellow colorations, respectively are produced. With this reagent about 0·15 μg of technetium can be detected.

Spectrophotometric determination of technetium and rhenium with potassium ferrocyanide

The success of potassium ferrocyanide as a qualitative reagent for technetium led to its investigation for the colorimetric determination of the element and, from preliminary studies, of rhenium also. The blue coloured complex of technetium was prepared and examined spectrophotometrically. This shows an absorption maximum at 680 mμ. As mentioned above, rhenium, under the same conditions, only produces a colour reaction with potassium ferrocyanide when reduced with bismuth amalgam in the presence of hydrochloric acid. In these circumstances a brownish-yellow complex is formed which, on examination spectrophotometrically, showed an absorption maximum at 420 mμ. The molar extinction coefficients were determined and found to be for technetium ~10,800, and for rhenium ~4000. The absorption spectra of both complexes are shown in Fig. 1. From this it will be seen that at the absorption maximum of technetium (680 mμ) there is zero contribution from rhenium (see Note below), so that technetium may be determined in the presence of rhenium without prior separation. Furthermore, the contribution of technetium to the extinction of rhenium at 420 mμ is small, and by preparing a correction curve of technetium concentration versus extinction at 420 mμ, it is possible to determine rhenium in the presence of technetium without prior separation. The influence of rhenium on technetium at 680 mμ, and that of technetium on rhenium at 420 mμ for different concentrations, are shown in Fig. 2 and Fig. 3.

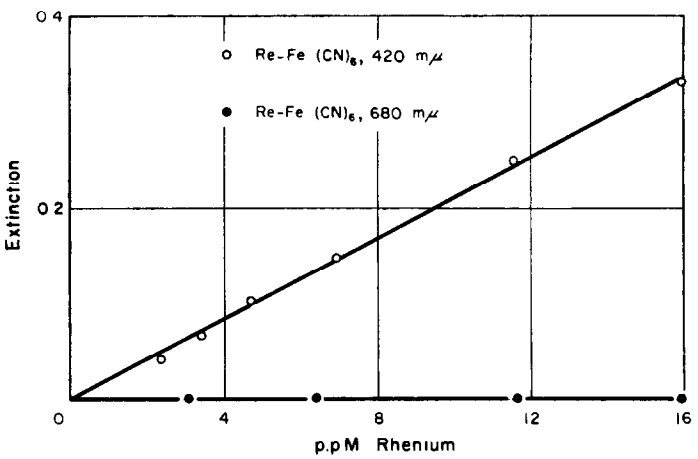


FIG. 2.—Influence of rhenium on technetium extinction.

EXPERIMENTAL

Apparatus and reagents

For the spectrophotometric investigations a Unicam spectrophotometer, SP600, was used with 1·000-cm silica cells.

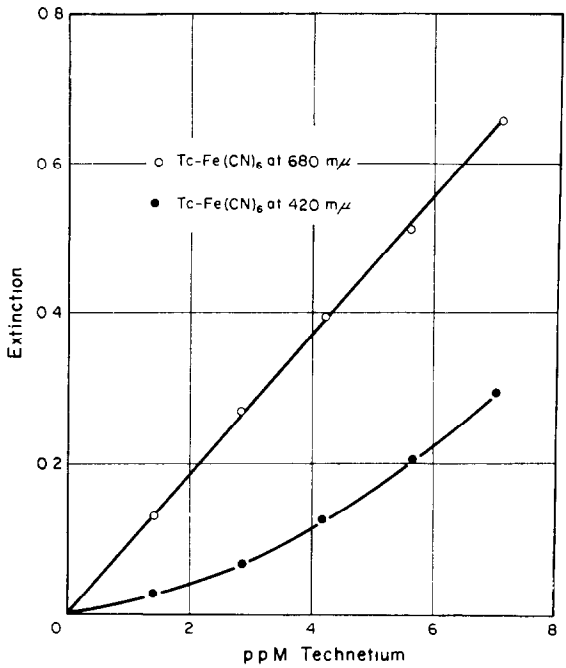


FIG. 3.—Influence of technetium on rhenium extinction.

Caesium pertechnetate: A standard aqueous solution containing 52 μg/ml and 4·5*M* in hydrochloric acid.

Potassium perrhenate: A standard aqueous solution containing 116 μg/ml of the "Specpure" compound in 4·5*M* hydrochloric acid.

Potassium ferrocyanide: A 5% aqueous solution of the AnalaR-grade reagent.

Bismuth amalgam[10]*:* Dissolve 3 g of granulated bismuth in 100 g of mercury in the presence of dilute sulphuric acid. Warm on a water bath and decant the amalgam.

Procedure

Place in a 30 ml separatory funnel 2 ml of 5·7*M* hydrochloric acid, and add to it a suitable aliquot of the test solution containing standard pertechnetate and perrhenate solutions. Add 2 ml of bismuth amalgam. It is advisable to wash the amalgam before use by shaking with several portions of 4·5*M* hydrochloric acid. Add 0·5 ml of 5% potassium ferrocyanide solution. Stopper and shake for 15 sec. Remove the amalgam, and allow the reduced solution to stand for 20 min in the dark.

Measure the extinction of technetium at 680 mμ and that of rhenium at 420 mμ. From a standard curve prepared from known amounts of the two elements, calculate the concentration of technetium and rhenium in the solution. It is desirable to correct by a blank carried through the same operations.

Note: If the concentration of rhenium is high, it can show a reading at the absorption maximum for technetium (680 mμ). In these circumstances the most effective procedure is to determine technetium without interference from rhenium by the Procedure 2.

Procedure 2

In a 5-ml volumetric flask place an aliquot of the test solution and add to it sufficient concentrated hydrochloric acid to make it about 4–6*M*. Add 0·5 ml of 5% potassium ferrocyanide, mix well and set aside for 30 min in the dark. Carry a blank through the same procedure.

Measure the extinction of the technetium blue at 680 mμ in a 1·000-cm cell. From a calibration curve determine the amount of technetium present. There is no interference from rhenium.

DISCUSSION

An attempt was made to elucidate the type of compound formed between the reduced perrhenate and potassium ferrocyanide. Attention was focussed on rhenium, to conserve technetium which is still, as far as we are concerned, a rare metal. The colour formed between perrhenate, stannous chloride and ferrocyanide is stable, can be extracted into solvents such as amyl alcohol, butyl alcohol and higher ketones. Its formation is strictly dependent on the acid concentration—at low acid concentration it is pale yellow, while at higher concentrations the yellow becomes pinker in appearance. The complex is readily sorbed on an anion-exchanger, suggesting that it is an anionic complex. Several experiments were carried out to find the molar ratio of rhenium to ferrocyanide. This was done by adding, in one experiment, an excess of rhenium to a known volume of ferrocyanide solution of the same concentration. In the second experiment an excess of ferrocyanide was added to the same quantity of rhenium as in the first experiment. In both experiments, the colour was developed in the usual way and the extinctions were measured at 470 mμ, where this complex showed an absorption maximum. The ratio of the absorbancies to the ratio of rhenium and ferrocyanide was found to be 3 : 1. This suggests that these two components form a type of double salt co-ordinated with hydrochloric acid molecules. With different acid concentrations the absorption maximum shifts along the wavelength axis.

If bismuth amalgam is used in place of stannous chloride, the complex produced has an absorption maximum at 420 mμ. This complex is also sorbed by an anion-exchange resin, and the colour is dependent on the acid concentration and ferrocyanide concentration. The optimum molarity of the acid is between 3 and 5, and the optimum potassium ferrocyanide concentration is $\sim$5%. The colour is time-dependent, full development occurring in 20–25 min.

From the information obtained about the complexes produced by stannous chloride and bismuth amalgam, it is suggested that with the former reagent in high acid concentration the perrhenate is first reduced to rhenium^{IV} and then forms a complex of the following type:

$$H_4[Fe(CN)_6 \cdot 3\ H_2ReCl_6 \cdot nHCl].$$

The reduction with bismuth amalgam is not so powerful, so that rhenium^{V} is produced which reacts with ferrocyanide to give a complex of the type:—

$$H_4[Fe(CN)_6 \cdot xH_2ReOCl_5 \cdot nHCl]$$

These may be compared with double salts of the type

$$(NH_4)_4[Fe(CN)_6] \cdot 2\ NH_4Cl \cdot 3\ H_2O,^{11}$$

and addition compounds with sulphuric acid $H_4[Fe(CN)_6] \cdot xH_2SO_4$ where $x = 5$ or 7.

As already mentioned, technetium with bismuth amalgam and ferrocyanide forms a blue complex. This is anionic in character, as shown by ion-exchange studies, and is probably similar in structure to the rhenium complex, the technetium first being reduced to the Tc^{V} or Tc^{VI} state with bismuth amalgam. (Technetium is more easily reduced than rhenium.) With stannous chloride in place of bismuth amalgam, technetium yields a yellowish-brown complex.

2. *Sulphosalicylic Acid*

Pertechnetate yields no colour with this reagent alone, but when first reduced with stannous chloride in an acid medium, a red colour is produced. The colour is stable for several days. $Iron^{III}$, rhenium, manganese and molybdate do not interfere with the test.

Spectrophotometric determination of technetium with sulphosalicylic acid

The complex formed between technetium and sulphosalicylic acid was examined spectrophotometrically. Fig. 4 shows the absorption spectrum of the complex. A

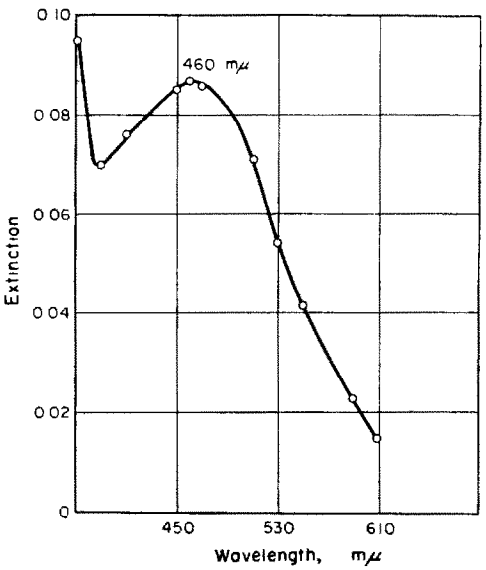


FIG. 4.—Absorption spectrum of technetium sulphosalicylate.

maximum occurs at wavelength 460 mμ. At this wavelength there is little or no interference from manganese, rhenium, molybdenum, thorium, iron or a number of other elements. It is possible to determine several μg of technetium in the presence of 3·0 mg of manganese, 0·2 mg of rhenium and 0·3 mg of molybdenum.

EXPERIMENTAL

Reagents

Stannous chloride solution: Dissolve 20 g of AnalaR stannous chloride dihydrate in sufficient 6*M* hydrochloric acid to dissolve the solid on warming. Dilute to 100 ml with 6*M* hydrochloric acid.

Sulphosalicylic acid: Dissolve 10 g of the acid in distilled water and dilute to 100 ml.

Buffer solution: Mix 97 ml of 0·2*M* hydrochloric acid and 50 ml of 0·2*M* potassium chloride (AnalaR) giving a solution of pH 1. Dilute to 200 ml with distilled water.

Procedure

To a 5-ml volumetric flask add 2 ml of buffer solution and an aliquot of pertechnetate solution. Add 0·5 ml of the sulphosalicylic acid reagent and 0·1 ml of the stannous chloride reagent. Mix thoroughly and dilute to the mark with buffer solution.

Measure the extinction of the orange-red solution after 30 min at 470 mμ in a 1·000-cm cell. From a standard curve calculate the amount of technetium present.

DISCUSSION

The complex is not extracted from aqueous solution by chloroform, amyl alcohol, toluene, or ether. This suggests that the technetium ion is co-ordinated with the hydroxyl oxygen and the carboxyl group, leaving the sulphonate group free.

The technetium is probably first reduced to the Tc^{V} state. The complex is moderately sensitive to acid concentration. The intensity decreases with increasing acid strength, probably because of a tendency of the complex to decompose at higher acidity. In the buffered solution the colour is, however, stable and maximum intensity occurs when the acidity is about 0·3*M*.

3. *α-Picolinic Acid*

α-Picolinic acid (pyridine-2-carboxylic acid), when added to pertechnetate, produces no colour, but on the addition of stannous chloride or ascorbic acid a red colour appears slowly. The reaction appears to be highly selective for technetium.

Spectrophotometric determination of technetium with α-picolinic acid

The complex formed between technetium and the reagent was examined spectrophotometrically. Fig. 5 shows the absorption spectra, with a maximum at 470-480 mμ

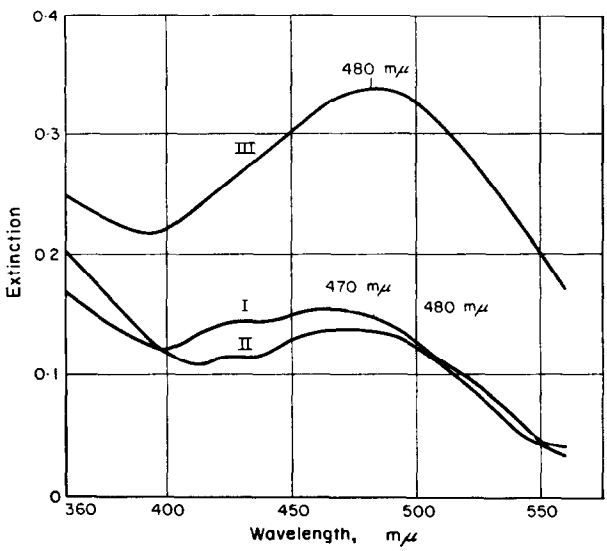


FIG. 5.—Absorption spectrum of technetium α-picolinate. I—After 20 min, 4·3 ppm of technetium: II—After 20 hr, 2·4 ppm of technetium: III—After 20 hr, 5.7 ppm of technetium.

At this wavelength there is interference from no element except molybdenum.

EXPERIMENTAL

Reagents

α-Picolinic acid: A 10% aqueous solution.

Ascorbic acid: A 10% aqueous solution.

Buffer solution: Prepare a KCl/HCl buffer solution of pH 2·0 from 10·6 ml of 0·2*M* HCl and 50 ml of 0·2*M* KCl, and dilute to 200 ml.

Procedure

In a 10-ml volumetric flask, place an aliquot of pertechnetate together with 5 ml of buffer solution, 0·5 ml of picolinic acid solution and 1 ml of ascorbic acid. Mix the contents well and place on a water bath maintained at 80° for 20 min. Cool, and dilute to the mark with buffer solution.

Measure the extinction of the yellow-red solution at 480 mμ against a blank treated in the same way. From a standard curve calculate the amount of technetium present.

DISCUSSION

If ascorbic acid is used as the reductant the solution shows a slightly more reddish tinge than when stannous chloride is used as reductant. The former shows a higher molar extinction coefficient of the order of 4400. The technetium is probably reduced to the 4- or 5-valent state by the reductants. Both species are partially extracted from aqueous solution by chloroform.

Zusammenfassung—Das Verhalten von Technetium und Rhenium gegenüber drei Reagentien: Kaliumferrocyanid, Sulfosalizylsäure und α-Picolinsäure wird diskutiert. Mit dem ersten Reagens formen Technetium und Rhenium in Gegenwart von Wismutamalgam oder Stannochlorid gefärbte Komponenten mit Absorptionsmaxima bei stark verschiednenen Wellenlängen. Dies gestattet dei Bestimmung beider Elemente in einer Lösung. Bis hinab zu 2 μg Technetium können derart bestimmt werden.

Pertechnat, nach Reduktion mit Stannochlorid, erzeugt mit Sulfosalizylsäure eine orangerote Färbung, was zur Bestimmung ausgewertet werden kann. Der Vorteil der Methode liegt darin, dass das Element in Gegenwart von ziemlich grossen Mengen von Rhenium, Mangan und Molybdän bestimmt werden kann.

Nach Reduktion mit Ascorninsäure gibt Pertechnat mit α-Picolinsäure eine rötlich-gelbe Färbung, die zur empfindlichen photometrischen Bestimmung herangezogen werden kann.

Die Typen der gebildeten Komplexe werden diskutiert.

Résumé—Les auteurs discutent du comportement du technétium et du rhénium en présence de trois réactifs: ferrocyanure de potassium, acide sulfosalicylique et acide α picolinique. Avec le premier réactif, le technétium et le rhénium, en présence d'amalgame de bismuth ou de chlorure stanneux, forment des solutions colorées qui ont une absorption maximale à des longueurs d'onde très différentes; celà permet le dosage spectrophotométrique des deux éléments l'un en présence de l'autre. On peut doser par cette méthode une quantité aussi faible que 2 μg de technétium.

L'acide sulfosalicylique donne avec le pertechnétate, qui a été réduit par le chlorure stanneux, une coloration rouge-orangé convenant pour le dosage de cet élément.

La méthode présente l'avantage suivant: l'élément peut être dosé en présence de très grandes quantités de rhénium, manganèse et molybdène.

Avec le pertechnétate réduit par l'acide ascorbique, l'acide α picolinique donne une solution jaune-rouge qui fournit une méthode très sensible de dosage spectro-photométrique de l'élément.

Les auteurs discutent le type de complexes formé avec ces réactifs.

REFERENCES

[1] C. Perrier and E. Segre, *J. Chem. Phys.*, 1957, **5**, 712.
[2] J. B. Gerlit, International Conference on the Peaceful Uses of Atomic Energy, A/Conf. 8. p. 671, U.S.S.R., 5th July, 1955.
[3] J. R. Embleton and J. K. Foreman, United Kingdom Atomic Authority, Production Group Report 93 (W), March, 1960.
[4] R. J. Magee, I. A. P. Scott and C. L. Wilson, *Talanta*, 1959, **2**, 376.
[5] C. E. Crouthamel, *Analyt. Chem.*, 1957, **29**, 1756.
[6] F. Jasim, R. J. Magee and C. L. Wilson, *Talanta*, 1960, **4**, 17.
[7] *Idem., ibid.*, 1959, **2**, 93.
[8] G. A. Barbieri, *Ber.*, 1927, **60B**, 2415.
[9] M. B. Tougarinoff, *Bull. Soc. Chim. Belge.*, 1934, **43**, 111.
[10] H. Spitzy, R. J. Magee and C. L. Wilson, *Mikrochim. Acta*, 1957, 354.
[11] H. Remy, *Treatise on Inorganic Chemistry*, Vol. II. Elsevier, Amsterdam, 1960, p. 281.

Talanta, 1962, Vol. 9, pp. 133 to 144. Pergamon Press Ltd. Printed in Northern Ireland

THE DETERMINATION OF INTERSTITIAL ELEMENTS IN THE REFRACTORY METALS

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Summary—A review is presented of current and potentially applicable methods for the determination of oxygen, nitrogen, hydrogen and carbon in molybdenum, tungsten, niobium, and tantalum.

INTRODUCTION

MOST of the material which follows was summarised from the files of the Defence Metals Information Centre and the open literature as of April, 1961. This brings up to-date an earlier DMIC review.[1]

The determination of the interstitials, oxygen, hydrogen, nitrogen and carbon, in the refractory metals, molybdenum, tungsten, niobium and tantalum, are most conveniently discussed when considered as to the interstitial element sought. This discussion follows such a system.

OXYGEN METHODS

A number of methods have been considered in connection with the determination of oxygen in molybdenum.[2] Where feasible for molybdenum, they can usually be applied with some modification to the other refractory metals. A number of possible methods are reviewed below.

Neutron activation

Thermal neutrons. In this method, the sample is irradiated with neutrons in a pile and the radiation emanating from the sample after irradiation is studied by suitable radiation counters. Unfortunately, oxygen has an almost zero cross-section to thermal neutrons. Therefore, the method is not suitable for oxygen, the most potent impurity in molybdenum. The method seems to offer some promise for the determination of hydrogen in metals and is excellent for detecting small amounts of rare earths.

Fast neutrons. Fast (14 MeV) neutrons have been used successfully for determination of oxygen in beryllium[3,4] and the method may prove satisfactory for molybdenum and the other refractory metals. The reaction produces protons and radioactive ^{16}N according to the equation, $^{16}O(n,p)^{16}N$. The ^{16}N decays with a half life of 7·4 sec by emission of β-rays with a maximum energy of 10 MeV (used for the oxygen analysis) along with high energy γ-rays.

Fluorination

This method has been applied to a number of metal oxides, salts[5] and titanium.[6]

In analysis, the sample is dissolved in bromine trifluoride by heating at 75° for 2 hr in a static vacuum. The reagent converts combined oxygen to free molecular oxygen according to the following reaction:

$$3\ MO_2 + 4\ BrF_2 \rightarrow 3\ MF_4 + 2\ Br_2 + 3\ O_2.$$

Oxygen is determined from pressure measurements after freezing out the other products and cooling the reaction tube to liquid-nitrogen temperature. In the case of some metals, nitrogen also may be released quantitatively. Oxygen is then determined from the drop in pressure observed when the oxygen-nitrogen mixture is passed over copper turnings at 400°. The residual pressure is due to nitrogen.

The method presumably can be applied to the determination of oxygen in niobium, tantalum and tungsten since no interference was found in the analysis of the oxides.[5] However, molybdenum oxide yielded a stable intermediate, $MoOF_4$, which is retained in the reaction medium.[6]

Other halogenation

Several other halogenation methods have been used for other metals and may prove workable for the refractory metals. The better known ones involve volatilisation of the metal by gaseous bromine, chlorine,[7] or hydrogen chloride[8] to leave oxygen as an oxide residue. The residue is weighed and the percentage of oxide in the residue estimated. Corrections are made for contaminants in the residue and for oxygen loss by reduction of oxide by the carbon content of the metal. The latter reaction was used as the basis of a modified method; that is, the bromination-carbon reduction method[9,10] in which all of the oxygen is converted to carbon monoxide and estimated as in the vacuum-fusion method. This method has been successfully used by several analysts. Bromination methods are not applicable to niobium and tantalum because volatile oxybromides are formed during the reaction. This prevents isolation of oxygen as a measurable species.

Fractography

Metallographic methods on polished sections of molybdenum are unsuitable because the amount of oxygen as inclusions appears to remain the same over rather wide composition ranges. Examination of a fractured surface is much more rewarding. Somewhere in the range 0·001 to 0·005% of oxygen, the oxide changes from discrete particles to a continuous sheet at the grain boundaries. Fractographs of specimens can be compared and their mechanical and other behaviour related to the impurity content without necessarily knowing the absolute amount of impurity in the samples. The fraction of the grain surface area covered with oxide is proportional to the oxygen content. This technique can be refined by using standards evaluated by primary analytical methods. Unfortunately, the method is not a quantitative one and in addition suffers several disadvantages. It is most useful for coarse-grained arc-cast molybdenum ingots. The grain size of most wrought molybdenum is too fine for fractographic methods to be most effective. Also the fracture obtained in samples of low oxygen content is nearly always transgranular so that it is hard to extend the fractographic method to very low oxygen contents. The method might be of some use for tungsten but would be of no practical value for niobium and tantalum which have higher oxygen solid solubilities.

Mass spectrometry

Mass spectrometry is not an independent method but an adjunct to a gas extraction method such as vacuum fusion.

The sensitivity of the mass spectrometer is such that 10^9 molecules per sec gives unit deflection. Unfortunately, the H_2O, CO, CO_2 and N_2 in which we are interested are the very gases normally present as residual gases in all vacuum systems, including that of the mass spectrometer. Hence, these gases are always background gases in the spectrometer, which reduces its sensitivity to them. Even so, the precision of $\pm 0{\cdot}0001\,\%$ on a 1-gram sample, which is believed desirable in analysing molybdenum, is 10 to 100 times the minimum sensitivity of the spectrometer. The advantage of using the spectrometer to analyse the gases evolved in vacuum fusion is that much smaller samples can be used and the identification of the gases is positive. The modern mass spectrometer can distinguish between carbon monoxide and nitrogen without difficulty. It should be emphasised that this method (mass spectrometer analysis of gases evolved by vacuum fusion) is *not* the isotopic dilution method which appears to involve the difficulties of both vacuum fusion and mass spectrometry.

Solid mass spectrometry

Solid mass spectrometry is a relatively new development which is capable of measuring very low concentrations. For example, rare earth metal impurities in graphite can be measured at levels of 0·01 atomic part per million. Unfortunately vacuum characteristics limit the detection of carbon, oxygen and nitrogen below 100 to 200 atomic parts per million. There is some possibility that hydrogen could be detected at lower levels.

Isotopic dilution

The method of isotopic dilution[11] is based on the equilibration of the sample's content of normal ($99{\cdot}757\,\%$ ^{16}O) oxygen with a known amount of oxygen enriched in ^{18}O as for example from a master alloy. Assuming that the extraction of oxygen-containing gas from the equilibrated complex is not affected by mass difference, only a fraction of the total gas need be removed to arrive at an assay of the total oxygen content. The extracted gas is analysed on a mass spectrograph to determine the degree of dilution of the ^{18}O during the equilibration. The original oxygen content of the metal sample can then be computed. The effect of ^{17}O enrichment does not seriously complicate the procedure. The method should be workable for niobium and tantalum at intermediate and high oxygen contents. Dilution and equilibration of oxygen in metals such as molybdenum and tungsten with low oxygen solubilities and containing precipitated oxides in the grain boundaries would seem to present insurmountable difficulties. Where applicable, the method is much more time-consuming and complicated than the vacuum-fusion method and certainly no more reliable.

Emission spectrometry

Emission spectrometry is a recent method now developed to a stage permitting consideration for application to most metals. To-date, it has been applied to niobium and tantalum.[12,13,14] A 100-mg specimen pressed into intimate contact with a small amount of platinum is arced in a graphite anode. Arcing is done in a chamber which is previously evacuated and filled with pure argon. The oxygen content of the specimen is evolved as carbon monoxide which is dissociated to atomic carbon and

oxygen. The lowest oxygen values obtained to date appear to be 20 ppm. Technique-wise the method is much simpler and faster than vacuum fusion. Potentially 70 to 80 specimens can be analysed in a day using a direct reader recording device.

Vacuum fusion

The familiar vacuum-fusion method[2] is the referee method for the determination of oxygen and hydrogen in most metals. It involves melting a metal sample in a graphite crucible in vacuum and collecting, measuring, and analysing the evolved gases. The extraction is usually made at 1600° or higher and the gas is principally carbon monoxide, hydrogen and nitrogen. Results are usually reported as percentages of oxygen, hydrogen, and nitrogen based on the weight of the metal sample.

Bath techniques. Individual metals require modification of the basic method. The refractory metals have melting points exceeding feasible operating temperatures for the vacuum-fusion furnace. To overcome this, specimens are sometimes dissolved in a degassed bath of another metal contained in the vacuum-fusion crucible. Iron,[15] iron-tin,[16] platinum,[17] platinum-tin,[18] or other metals are used. Extraction temperatures with a platinum bath may be as high as 2000°. It is essential that the bath dissolve carbon to reduce oxides and not form higher melting point intermetallic compounds at concentrations up to at least 10 weight % of the specimen metal.

Flux techniques. Sometimes refractory metals are melted by dropping the specimen and the fluxing metal simultaneously into the graphite crucible. The flux is usually tin or platinum and preferably is in intimate contact with the specimen. The specimen may be imbedded in the flux by pressing or may be wrapped in the flux. In the case of titanium,[19] the specimen and tin flux are dropped onto a bed of graphite chips contained in the crucible. This permits dispersion of the specimen in thin layers in intimate contact with graphite and aids the reduction of the oxygen of the titanium. The metal soon solidifies because of evaporation of the tin and the gradual conversion of the titanium to the high-melting carbide. The last gas removed is often released by diffusion-extraction from the solid.

The platinum flux[20] technique requires no graphite chips and has the advantage that the residue remains molten throughout the gas extraction.

Gas separation and identification. The gas extracted in the vacuum-fusion method is analysed in a number of ways. Low pressure analysis through absorption by dry chemicals or through fractional freezing are most commonly used. The gas also can be analysed by mass spectrograph, wet chemical (Orsat) apparatus, gas chromatograph, and other means.

Inert-gas fusion

In the inert-gas fusion method, an inert gas is purified and passed over an inductively heated graphite crucible (in a reaction tube) containing the sample. Oxides in the sample are reduced to carbon monoxide and are carried by the inert gas through an oxidising agent. The carbon dioxide thus formed is then measured in a conductivity cell where the change in resistance is read. This change is translated to % of oxygen by means of a graph prepared from results on primary standards. At oxygen levels below 100 ppm this method has limitations. Estimates of sensitivity range from 5 to 10 ppm oxygen on a 1-g sample. The measurement is indirect and requires repeated calibration. There is some indication of trouble caused by variation of the oxygen

content of the platinum flux used with low oxygen niobium. This difficulty may be overcome by using a bath technique. No measurement of nitrogen or hydrogen is obtained by this method. A commercial apparatus for inert-gas fusion is sold by LECO, Laboratory Equipment Corporation, St. Joseph, Michigan.

Practical Application of Oxygen Methods

Molybdenum

A vacuum-fusion iron bath technique[2,15] for oxygen in molybdenum was developed in the course of a co-operative study of this analysis through the Office of Naval Research Advisory Committee on Molybdenum. Work was done through a sub-committee on the Analysis for Gases in Molybdenum. Recommended details of the technique were that:

(1) Graphite parts (crucibles, *etc.*) be halogen purified.
(2) Extraction be carried out for a minimum of 20 min.
(3) Extraction temperature be 1600 to 1650° to avoid the solidification of the bath experienced at higher temperatures.
(4) Molybdenum content of the bath be limited to 30 weight %.

On molybdenum containing about 60 ppm of oxygen, the reproducibility within several individual laboratories was to $\pm$ 2 ppm. However, laboratory averages ranged from about 40 ppm to 70 ppm. Recovery seemed to increase as the operator gained experience with the technique. Work by the same group with molybdenum containing about 10 ppm of oxygen showed greater relative variation. Need for further study at this level was indicated.

More recently the work on molybdenum was continued under the guidance of the Task Group on Oxygen in Molybdenum, Division M, Committee E-3, ASTM. The most recent meeting of the Task Group was held at Westinghouse Research Laboratories, November 19 and 20, 1959. Results obtained with an iron-tin bath were discussed. The analytical specimens were of the same high- and low-oxygen molybdenum studied with the iron bath. This time the results for the high-oxygen molybdenum ranged from about 60 to 80 ppm oxygen and averaged close to 70 ppm. The statistical significance of the data is presently being determined. The higher average is probably caused by the greater experience of the analysts rather than to any slight difference in analytical method entailed with the addition of tin to the bath. The low-oxygen molybdenum gave laboratory averages from 3 to 11 ppm and averaged about 8 ppm. It was concluded that results at the 60 or 70 ppm level are reasonably satisfactory but better reproducibility is needed below the 10 ppm level. It was agreed to prepare a description of the iron-tin method to submit to the ASTM for consideration. The outline of the method is as follows. Use a 2-g sample cleaned by filing. Degas the graphite crucible at 2350°. About 2 hr is required. Reduce temperature to 1650° and take a 30-min blank, then drop 10 g of iron and 0·3 g of tin to form a bath. Degas for a minimum time to obtain a satisfactory blank. Drop sample and extract gas for 30 min. Drop 0·3 g of tin between samples. If tin has a measurable oxygen content, degas before dropping the molybdenum sample. Periodically drop additional iron between samples to keep the molybdenum concentration of the melt below 30 weight %. Analyse the extracted gas.

One of the laboratories (Bureau of Mines, Boulder City) of the Task Group used a bath of 80 platinum–20 tin and a bath temperature of 1650°. This takes advantage

of the eutectic in the platinum-tin system (72 Pt: 28 Sn, 1080°). The bath is quite fluid and the tin content is said to be quite stable and not readily lost by vaporisation. The platinum is degassed above its melting point and the temperature dropped to 1650° before adding tin. The Task Force proposes a future investigation of this technique.

Earlier, a platinum bath at 1850° was used by Wilkins.[2] Iron was added to the platinum bath before the introduction of molybdenum samples.

A diffusion-extraction technique was used by Fagel, Witbeck and Smith.[21] In this method the solid sample is heated in a degassed graphite crucible in a vacuum-fusion apparatus. Oxygen diffuses to the surface of the specimen and is released as carbon monoxide. Nitrogen and hydrogen are also evolved. The extracted gases are analysed as in the vacuum-fusion method.

The LECO conductimetric oxygen analyser (inert gas fusion apparatus) is reported by the company to have been used to analyse for oxygen in molybdenum, tungsten, tantalum and niobium.

Several other papers[22,23,24,25] on the determination of oxygen in molybdenum have appeared. Most deal with versions of the iron bath technique which differ only in detail with descriptions already given.

Tungsten

The methods for the analysis of molybdenum are often used without modification for the analysis of tungsten. The principal methods reported are the iron bath,[21,23] diffusion extraction[21] and inert gas fusion.[26] The concentration of tungsten should not exceed 30 weight % in the iron bath.[24] The volume of extracted gases is the same at 1650° as at 1800°, but the 1650° results are more reproducible.[23]

The National Research Corporation[27] has reported the use of a platinum bath at 1850° for determining oxygen in tungsten. Samples weigh about 0·5 g and several are run in a 25 to 30 g platinum bath.

Niobium

Oxygen in niobium has been determined by the emission spectrographic method. Success was achieved by fluxing the sample with platinum.[12,13]

A diffusion extraction method for niobium was developed by Hansen and Mallett.[28] Oxygen as carbon monoxide is quantitatively removed from a 0·3-g sample at 2000° in vacuum in 30 min. The sensitivity of the method was about 20 ppm for this size of sample.

The LECO inert gas fusion method[26] has also been used for this analysis. A sensitivity of 2 ppm for a 1-g sample is claimed. The temperature of extraction is about 2200°.

The vacuum-fusion method for niobium has been described by at least two investigators.[23,29] The conditions specified by Harris[29] include the use of 0·25-g samples melted in a platinum bath (weight not specified) at 1950°. Complete gas extraction required only 10 min. A probable sensitivity of 5 ppm is reported.

Mikhailova *et al.*,[23] used the same vacuum-fusion procedure as for molybdenum and tungsten. Extraction was made with an iron bath at 1650°.

Benner[30] lists the use at 1850° of both the iron bath and the platinum bath for the analysis of niobium.

In June, 1959, the Oxygen Sub-Group, Niobium Task Group, Division M, Committee E-3, ASTM, met to discuss the results of an interlaboratory round-robin study[31] of the analysis of niobium for oxygen. The test specimens were prepared from niobium ingots, hot rolled at 1200° to 5/8 inch, round surface ground to remove oxide and cold forged to 1/4 inch round. It was concluded that a method worthy of write-up for consideration by ASTM had been achieved. Results based on an average value from each of nine laboratories, seven by vacuum fusion and two by inert gas fusion, averaged 299 ppm of oxygen with a standard deviation of 17 ppm; the coefficient of variation was 5·8%. In vacuum fusion most of the laboratories used platinum either as a flux dropped with the sample or as a bath or a combination of flux and bath. Extraction temperatures ranged from 1790 to 1950° and extraction times from 10 to 50 min. It appears that 1900° for 15 min could be recommended. It was generally agreed that the niobium content of the bath should not exceed 20 weight %.

One laboratory used a nickel bath at 1800° with a 10-min extraction time. Again the niobium concentration was limited to 20 weight %.

The Task Group members using the inert gas-fusion method extracted the gas in 6 to 10 min at 2200°. A platinum bath and iron bath plus a 1:1 platinum flux was used.

Tantalum

Direct references to methods of determining oxygen in tantalum are fewer than for the other refractory metals. Good results by the inert gas fusion,[26] the diffusion extraction[21] and emission spectrographic[13] methods are reported.

Beach and Guldner[16] analyse tantalum by the same vacuum-fusion iron-tin bath technique used by them for molybdenum. A 2-g sample is dropped into a bath containing initially 6 g of iron and 0·3 g of tin. Intermittent additions of iron are made to keep the iron content between 25 and 40 weight %. Each sample is wrapped in 0·3 g of tin sheet before dropping.

It is interesting that Smiley[32] using perhaps the earliest form of the inert gas fusion technique (his capillary-trap technique) found the platinum bath did not work for tantalum (molybdenum, tungsten and niobium). Recent unpublished work at Battelle indicates that the use of a platinum-bath vacuum-fusion technique yields excellent and rapid results. Gas extraction is complete in 5 min at 1850°. Up to 50% of tantalum can be tolerated in the bath. For a 1-g sample the usual sensitivity of the analysis is 7 ppm. For total gas contents below 100 μl (equivalent to 70 ppm of oxygen for a 1-g sample), a sensitivity of 0·2 ppm is realised.

HYDROGEN METHODS

The determination of hydrogen in metals is considered to be simpler than the determination of oxygen and nitrogen. Hydrogen is removed rapidly and quantitatively from nearly all metals when melted in vacuum. Thus good hydrogen results are often obtained in the trial of unsuccessful vacuum-fusion techniques for oxygen. The Serfass Gas Analyser[33] which utilises a specially designed palladium diffusion valve appears particularly well suited to the rapid determination of hydrogen alone by vacuum fusion. A sensitivity of 0·2 ppm is indicated.

Hydrogen is also readily removed by diffusion from solid samples. The most satisfactory extraction rates are obtained at 1000° and higher. In the case of titanium,

extractions are made at 1350° for 20 min and the evolved gas is relatively pure hydrogen. For practical purposes the gas need only by measured (not analysed). Benner[30] reports the use of a molybdenum bucket in vacuum at 1400° for hydrogen extraction from titanium and zirconium in 2 to 3 min. The sensitivity of the analysis is about 2 ppm at the 50 to 100-ppm level. There is no apparent reason why this technique should not be directly applicable to the refractory metals. If other gases are evolved, the hydrogen is readily separated by diffusion through a heated palladium tube. The hydrogen content of the gas can also, of course, be determined by conventional oxidation and absorption techniques, or by thermal conductivity, mass spectrometry, or gas chromatography techniques.

The equilibrium pressure method applied by McKinley[34] to titanium would appear also applicable to tantalum and niobium. However, the method would probably lack sensitivity in the low concentration range, for it is based on the amount of gas evolved in a closed system at a constant temperature (1050° for titanium). When an equilibrium pressure is reached, the volume of gaseous hydrogen is calculated. The volume of hydrogen remaining in the metal at this pressure is computed from experimental equilibrium data for the metal. The total hydrogen is a summation of these two volumes.

A tin bath method[35] has been used for steels. The sample is dissolved in tin at 1100 to 1200° and the hydrogen is readily evolved and measured. Only minor amounts of other gases are evolved. It is unlikely that such low-temperature fluxing of the refractory metals will be found possible.

A combustion method in which the sample is ignited in oxygen in the presence of a flux[36] has been used for titanium. The method was never widely used because it is cumbrous compared to other methods.

Specific references to the determination of hydrogen in refractory metals by vacuum fusion were made by Hansen and Mallett (molybdenum),[2] Mikhailov *et al.* (molybdenum, tungsten, niobium)[23] and Henry and Sloman (molybdenum).[25]

Hydrogen values (molybdenum, tungsten, niobium) were obtained by Fagel *et al.*,[21] in the course of diffusion extraction at 2000° for oxygen. Results by emission spectroscopy (niobium) were reported by Fassel.[12,13]

NITROGEN METHODS

The following discussion of the solution distillation method used at Battelle for the determination of nitrogen in refractory metals was prepared by Chase.[37,38]

Solution-Distillation Method

When determining nitrogen in niobium-, tantalum-, molybdenum- and tungsten-base alloys, the major problem is in the digestion and complete dissolution of the samples. Depending upon the type and quantity of alloying elements present various digestion procedures must be used. In general, one tries to avoid using an acid that will produce an insoluble film or residue with any major element in the alloy.

The following procedures have proved useful in dissolving the above metals in the pure state or alloyed with metals having similar solubilities.

Molybdenum and molybdenum alloys

Transfer a 0·5 to 1·0-g sample to a 30-ml micro-Kjeldahl flask. Add 6 ml of 1:1 sulphuric acid and 1 ml of 60% phosphoric acid. Heat on the digestion rack until the excess water is driven off and the

acid refluxes about half way up the neck of the flask. Continue digestion until no residue remains.

Niobium, tantalum, tungsten and their alloys

Transfer a 0·5-g sample to a 40-ml platinum crucible. It is desirable to have the sample in the form of >40 mesh chips. Add 5 ml of 1:1 sulphuric acid along with 2 ml of hydrofluoric acid and 1 ml of 30% hydrogen peroxide. Cover with a platinum lid and heat on a hot plate until the major part of hydrofluoric acid is driven off. If a residue remains, repeat the additions of hydrofluoric acid and hydrogen peroxide and continue heating until all of the sample has reacted. Also, one must make sure that all of the hydrogen peroxide has decomposed before proceeding to the distillation.

Regardless of the type of acid attack on the samples, the following procedure is applicable.

Apparatus and reagents

Distillation apparatus. The Parnas-Wagner apparatus is modified by the addition of an electrically heated steam generator consisting of a 2-litre reaction vessel with immersion heater and a three-way stopcock placed between steam generator and still. This allows the steam to be exhausted to the drain while the still empties without interrupting the heat supply.

38% *Sodium hydroxide solution:* Dissolve 1·5 lb of sodium hydroxide in 2 litres of distilled water, add 1·0 g of Devarda's alloy, and boil until the volume is 1800 ml.

Mixed indicator solution: Dissolve 0·0166 g of methyl red and 0·0834 g of bromocresol green in 100 ml of neutral ethanol.

Boric acid solution: A stock solution is made up by dissolving 40 g of C.P. boric acid in 1000 ml of tepid water. A dilute boric acid solution is prepared by diluting 40 ml of the 4% solution to 1000 ml with water.

Standard sulphuric acid: Make up a stock solution of sulphuric acid of approximately 0·07*N*. The stock solution is diluted to 0·007*N* for the determination of nitrogen in the range of 0·001 to 0·100%. For samples above 0·100% in nitrogen use the 0·07*N* sulphuric acid.

Procedure

Transfer the diluted sample solution to the Parnas-Wagner still and add 25 ml of sodium hydroxide solution. Distil and collect the condensate in a 50-ml Erlenmeyer flask containing 4 drops of mixed indicator solution and 10 ml of dilute boric acid solution. For samples containing more than 0·100% of nitrogen, use 10 ml of 2% boric acid solution as the ammonia collector. Adjust the heat input by a variable transformer so that 5 min after distillation begins, 10 ml of condensate will have been collected.

Titrate the collected ammonia with standard acid, and make a blank determination using the same amounts of all reagents as in the sample determination. An alternative method used by others[39] is to determine the ammonia in the condensate spectrophotometrically with Nessler's reagent.

Alkali-Fusion Method

Harris of the Westinghouse Research Laboratories analysed niobium for nitrogen[29] by an alkali-fusion method previously used in that laboratory for the analysis of boron, tungsten and molybdenum.[40] The fusion apparatus consists of a Vycor tube, 30 inch long and 1–1/4 inch in diameter, fitted with ground glass joints at each end and tubes for the passage of carrier gas. A nickel boat containing a fusion mixture is placed inside a nickel sleeve which protects the combustion tube from spattered alkali. The mixture is heated with a 12-inch split-tube furnace.

The niobium, in the form of fine powder or millings, is fused with sodium hydroxide at 600° for 1-0·5 hr in a slow stream of hydrogen. The ammonia formed during the fusion is absorbed in water or boric acid and determined by the usual titrimetric or colorimetric techniques. A blank is determined in the same way. Blanks as low as 1 μg can be obtained by prefusing the sodium hydroxide before use. Otherwise, the blank amounts to 20 to 25 μg of nitrogen which may be tolerable at high nitrogen levels.

Other Methods

The vacuum diffusion-extraction was developed for molybdenum by Mallett and Griffith.[15] Extraction was made at 1800° for 30 to 50 min. The same method at 2000° for 20 to 30 min was used for molybdenum, tungsten and tantalum by Fagel, Witbeck and Smith.[21] Other methods include the use for one or more of the refractory metals, of the vacuum fusion iron bath,[23,25] iron-tin bath[21] and the emission spectrograph.[13] In general, vacuum-fusion nitrogen values for metals other than steels amount to no more than numbers obtained incidental to oxygen determinations. The findings were never properly verified by work with standards. A steel containing 0·89% of titanium yielded only half the solution-distillation value.[41] For chromium and its alloys, nitrogen (vacuum fusion) recovery approaches 80%. In the case of titanium, no nitrogen is recovered by the dry-crucible (tin flux) technique. The platinum bath technique has yielded some apparently satisfactory results but the conclusion[42] is that the "vacuum-fusion technique, as at present operated, does not furnish very reliable nitrogen figures for those elements forming very stable nitrides." No concentrated effort has been made to determine the conditions required for quantitative recovery of nitrogen from refractory metals by vacuum fusion.

It appears that wet chemical methods may be adequate for determining nitrogen levels above 10 or 20 ppm. No method exists for levels lower than this.

CARBON METHODS

The determination of carbon in metals is normally carried out by a combustion technique in which the carbon is converted to carbon dioxide for measurement. The three most common methods[37,38] of measurement and their areas of application are as follows.

Gravimetric procedure

In this method the sample, with appropriate flux, is combusted in a Globar furnace. The resulting carbon dioxide, after removal of impurities, is collected and weighed in an absorption bulb containing Ascarite. The working detail can be found in such standard works as *ASTM Methods of Chemical Analysis of Metals* or Scott's *Standard Methods of Chemical Analysis*. At Battelle, the gravimetric method is usually reserved for those samples containing more than 1% of carbon.

Gasometric procedure

The combustion step is carried out just as in the gravimetric procedure. The gas mixture from the combustion, after the removal of impurities, is collected and measured in a gas burette. The carbon dioxide is then removed from the gas mixture by absorption in potassium hydroxide solution. The volume of gas is measured again and from the loss in volume one can calculate the carbon content of the sample. The method is rapid and reliable, and the working details can be had from the manufacturers of such apparatus. This procedure is most useful in determining carbon contents of from 0·03 to 2·0 %.

Conductometric procedure

This is a modification of a method reported by Bennet, Harley and Fowler[43] for

the determination of carbon in steel. This procedure is useful in the range of from 5 to 400 ppm of carbon. Since, presently, most interest is centered in metals and alloys in this range of carbon content, this method will be described more fully.

In the conductometric determination of carbon, a sample is combusted in pure oxygen in a high-frequency induction furnace, and the amount of carbon dioxide resulting is established by measuring the change in conductivity of a barium hydroxide solution in which the carbon dioxide is adsorbed. A commercial apparatus using these principles is manufactured by Laboratory Equipment Corporation. Full operating details may be obtained from the manufacturer.

In determining the carbon content of niobium, tantalum, molybdenum, and tungsten by the conductometric technique, the main difficulty is in obtaining a quantitative combustion. These metals and their alloys do not properly load the induction coil, and an incomplete combustion results. To overcome this difficulty, the use of several different combustion accelerators has been proposed. High-purity iron and tin are most widely used for this purpose and have been found satisfactory for the metals and alloys mentioned above. Since these materials contain small amounts of carbon and therefore introduce a significant blank value, they must be used with intelligence. One must use sufficient accelerator to ensure complete combustion, but avoid excessive amounts and their attendant high blank values.

For most metals of this type, one may use a 1-g sample along with 1 g of high-purity iron and 1 g of C.P. tin. The tin has such a low blank that it need not be weighed, but simply measured out with a small scoop. For those samples which are still more difficult to burn, one may use a 0·5-g sample with 1 g of iron plus 1 g of tin. For those materials more easily burned, one may cut the amount of iron to 0·5 g with 1 g of sample and 1 g of tin. To test for complete combustion, the cooled melt may be broken up with a hammer and examined for unburned metal under a low-power magnifier.

Finally, in the determination of low amounts of carbon in metals one of the most important and sometimes overlooked precautions is cleanliness. Since carbon in its many forms is such a common contaminant, one must keep the apparatus and its surroundings as clean as possible. Equally important, it must be impressed upon all who handle the sample in its various stages of preparation that the analysis is only as good as the weakest link in the chain of sample preparation.

Zusammenfassung—Eine Übersicht über die derzeitigen Methoden zur Bestimmung von Sauerstoff, Stickstoff, Wasserstoff und Kohlenstoff in Mo, W, Nb, und Ta wird gegeben.

Résmué—L'auteur présente un compte-rendu des méthodes électrochimiques applicables au dosage de l'oxygène, de l'azote, de l'hydrogène et du carbone dans le molybdène, le tungstène, le niobium et le tantale.

REFERENCES

[1] M. W. Mallett, PB 161 199, DMIC Memo. 49, March 31, 1960, Defense Metals Information Centre, Battelle Memorial Institute, Columbus, Ohio.
[2] W. R. Hansen and M. W. Mallett, *Determination of Gases in Molybdenum, The Metal Molybdenum*, J. J. Harwood (Editor). American Society for Metals (1958), Chapter 16, p. 365.
[3] R. F. Coleman and J. L. Perkin, *Analyst*, 1959, **84**, 233.
[4] R. F. Coleman, Special Report No. 68, The Iron and Steel Institute, 1960, p. 93.
[5] H. R. Hoekstra and J. J. Katz, *Analyt. Chem.*, 1953, **25**, 1608.
[6] W. A. Dupraw and H. J. O'Neill, *Analyt. Chem.*, 1959, **31**, 1104.

[7] J. A. Corbett, *Analyst*, 1951, **76,** 652.
[8] Proceedings of the Symposium on Analysis and Metallography of Titanium, Armour Research Foundation, Chicago, Illinois, 1951, June p. 17.
[9] M. Codell and G. Norwitz, *Analyt. Chem.*, 1955, **27,** 1083.
[10] M. Codell, S. Kallman and G. Norwitz, Symposium on Determination of Gases in Metals, ASTM Special Technical Publication No. 222, American Society for Testing Materials, 1958, p. 33.
[11] A. V. Grosse, A. D. Kirschenbaum and R. D. Mossman, *Trans. Amer. Soc. Metals*, 1954, **46,** 525.
[12] Semiannual Summary Research Report in Chemistry [Spectroscopy] ISC-1049, Ames Laboratory at Iowa State College, USAEC Research and Development Report, 1958, November 1.
[13] V. A. Fassel, W. A. Gordon and R. J. Jasinski, Second United Nations International Conference on the Peaceful Uses of Atomic Energy, A/Conf. 15/P/917, U.S.A., 1958, June.
[14] V. A. Fassel, W. A. Gordon and R. W. Tabeling, ASTM Special Technical Publication No. 222, American Society for Testing Materials, 1958, p. 41.
[15] M. W. Mallett and C. B. Griffith, *Trans. Amer. Soc. Metals*, 1954, **46,** 375.
[16] A. L. Beach and W. G. Guldner, Symposium on Determination of Gases in Metals, ASTM Special Technical Publication No. 222, American Society for Testing Materials, 1958, p. 15.
[17] J. N. Gregory and D. Mapper, *Analyst*, 1955, **80,** 230.
[18] T. D. McKinley, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 1959.
[19] D. I. Walter, *Analyt. Chem.*, 1950, **22,** 297.
[20] W. R. Hansen, M. W. Mallett and M. J. Trzeciak, *ibid.*, 1959, **31,** 1237.
[21] J. E. Fagel, R. F. Witbeck and H. A. Smith, *ibid.*, 1959, **31,** 1115.
[22] E. W. Balis, J. E. Fagel Nr. and R. S. McDonald, *ibid.*, 1955, **27,** 1632.
[23] G. V. Mikhailov, Z. M. Turovtseva, R. Sh. Khaltov and V. I. Vannadsky, *Zhur. analit. Khim.*, 1957, **12,** 338.
[24] H. A. Sloman, *Metallurgia*, 1945, **32,** 223.
[25] C. E. Henry and H. A. Sloman, *J. Inst. Metals*, 1951, **80,** 391.
[26] *Conductimetric Oxygen Analyzer for Ferrous and Nonferrous Metals and Alloys.* Laboratory Equipment Corporation, St. Joseph, Michigan, (1959).
[27] Private communication.
[28] W. R. Hansen and M. W. Mallett, *Analyt. Chem.*, 1957, **29,** 1868.
[29] W. F. Harris, *Technology of Columbium (Niobium)*, The Electrochemical Society. John Wiley and Sons, Inc., New York, 1958, p. 57.
[30] F. C. Benner, *Analytical Techniques for Vacuum Processed Metals and Alloys, Part IX, Analytical Techniques.* Vacuum Metallurgy, R. F. Bunshah (Editor), Reinhold Publishing Corporation, New York, 1958, Chapter 27, p. 407.
[31] T. D. McKinley, Report of Oxygen Subgroup, Niobium Task Force, Division M, Committee E-3, ASTM, June 23, 1959 (Revised August, 1959).
[32] W. G. Smiley, Symposium on Determination of Gases in Metals, ASTM Special Technical Publication No. 222, American Society for Testing Materials, 1958, p. 25.
[33] *Serfass Gas Analyzer.* Fisher Scientific, 101 Fisher Building, Pittsburgh 19, Pennsylvania, October, 1957.
[34] T. D. McKinley, *J. Electrochem. Soc.*, 1955, **102,** 117.
[35] D. Carney, J. Chipman and N. J. Grant, *Trans. AIME*, 1950, **188,** 397.
[36] M. Codell and G. Norwitz, *Analyt. Chem.*, 1956, **28,** 610.
[37] D. L. Chase, private communication.
[38] F. E. Huber and D. L. Chase, *Chemist-Analyst*, 1961, **50,** 71.
[39] G. W. Goward and E. F. Tretow, Westinghouse, Bettis Plant, April 24, 1956, WAPD-CTA-(GLA)-203, UC-4. Unclassified, available from OTS.
[40] E. W. Beiter, F. P. Byrne, W. F. Harris, M. I. Mistrik and R. H. Wynne, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 1957.
[41] N. F. Beeghly, *Analyt. Chem.*, 1952, **24,** 1097.
[42] E. Booth, F. J. Bryant and T. Parker, *Analyst*, 1957, **82,** 50.
[43] E. L. Bennet, J. H. Harley and R. M. Fowler, *Analyt. Chem.*, 1950, **22,** 445.

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THE FLAME PHOTOMETRIC DETERMINATION OF LEAD IN LEAD ALLOYS

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Summary—Methods are described for the determination of lead in lead alloys by flame photometry. The samples analysed contained from 4 to 85% of lead and the results obtained were reproducible to ±5% of the amount of lead present. The analyses were accurate to within ±5% of the lead content.

LEAD exhibits weak emission lines in the mantle of an oxygen-fuel flame and the emission at 405·8 mμ has been successfully applied to the determination of tetra-ethyl lead in gasoline.[1–3] This lead line is subject to spectral interference from manganese and potassium, but if necessary this interference can be avoided by using the lead line at 368·3 mμ.[4]

The lead line at 283·3 mμ has been used together with the atomic absorption spectrophotometric technique by Elwell and Gidley[5] for the determination of lead in copper-base alloys and steel and by Robinson[6] for the determination of lead in gasoline.

The determination of lead in alloys by simple flame photometry has not received much attention because of the very low emission sensitivity of the lead lines. The studies described in this paper indicate the precision and accuracy that may be obtained in alloy analysis using this technique.

EXPERIMENTAL AND RESULTS

Equipment

The apparatus used consisted of a Hilger H700 Uvispek Spectrophotometer fitted with a Hilger H868 Flame Photometer attachment.

In accordance with the manufacturer's instructions, the oxygen-hydrogen flame was fed with oxygen at a pressure of 30 lb/sq. in. and hydrogen at a pressure of 20 lb/sq. in.

The emission of the most sensitive lead line, *i.e.*, 405·8 mμ, was measured using the normal UV photocell with the ×5 amplification switch in operation. The width of the slits was adjusted to 0·15 mm (corresponding to 0·5 mμ), and the flame photometer mirror was adjusted to give maximum signal.

Correction for flame background was made by adjusting the instrument zero with the shutter open while distilled water was sprayed into the flame. The "check" (or 100% transmittance) adjustment was then made by spraying a standard lead solution of concentration greater than that of the samples to be tested into the flame. The intensity of emission from the standard lead solution was thus made to correspond to the 100% reading of the transmittance scale on the instrument. This scale was then used to measure the emission intensity of test solutions relative to the intensity of the standard solution in terms of "% transmittance". The constancy of the "zero" and "check" settings was used as a guide to the reproducibility of the flame conditions and rate of atomisation. In most cases, variations in these settings were traced to partial clogging of the capillary sampling tube.

Multiple readings of the percentage transmittance of test samples were then made, with constant checking of the "zero" and "check" adjustments.

Selection of concentration limits

Because of the low emission sensitivities of the lead lines, high concentrations of lead are required in the test solutions. For the 405·8 mμ line, Dean[4] reports a sensitivity of 14 ppm of Pb per % transmittance, which indicates that the check or 100% transmittance standard should contain at least 1400 ppm of Pb.

A standard solution of lead nitrate containing 2000 ppm of Pb was prepared by dissolving 1·598 g of AnalaR $Pb(NO_3)_2$ in 500 ml of distilled water. Standards containing lower concentrations of lead were prepared by dilution of this stock solution.

The % transmittance of a series of the diluted standards were then measured using the 2000 ppm of Pb solution as the "check" standard. A plot of % transmittance *versus* concentration of lead yielded a straight line. Erratic results were obtained when the measurements were repeated using the 1000 ppm of Pb solution as "check" standard. It therefore appears that the emission sensitivity of lead using the Hilger apparatus, is of the same order as that observed by Dean. Thus in all subsequent studies the concentration of lead in the check solution was kept greater than 1400 ppm.

For *direct measurement*, *i.e.*, where the content of lead in the unknown is calculated from the relationship

$$\text{ppm of Pb}_{(\text{unknown})} = \%T \times 10^{-2} \times \text{ppm of Pb}_{(\text{check})}, \quad (1)$$

the concentration of lead in the unknown should preferably be just slightly less than the concentration of lead in the "check" standard solution. Apart from reducing any effects from self-absorption of radiation, this condition also reduces the % error in the final result introduced by any error in measurement of emission. For example, curve A in Fig. 1 represents the possible % error that may be obtained in the final result with samples giving different transmittance readings, assuming that there is a 1% error in the actual transmittance reading. It is obvious from this curve that the concentration of lead in the unknown solution should be large enough to yield a reading of at least 40% transmittance. This, with a minimum concentration of 1400 ppm of Pb in the "check" standard, corresponds to 550 ppm of Pb. If the test solution is prepared by dissolving 1 g of alloy and diluting to 100 ml, this 550 ppm of Pb corresponds to 5·5% of Pb in the alloy. The method therefore appears to be mainly suitable for alloys containing an appreciable content of lead.

In the analysis of metal alloys, difficulty arises in preparing standard "check" solutions of composition comparable to that of the assay solution. In these circumstances, a method based on the *standard*

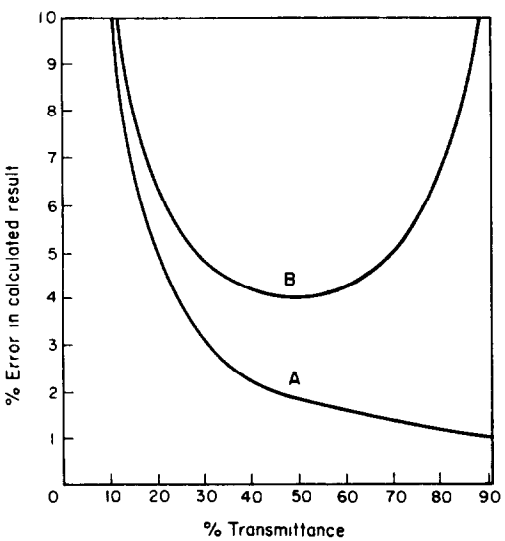


FIG. 1.—Percentage error introduced into calculated lead content of sample by 1% error in transmittance reading.
Curve A: Assay measured directly against a standard lead solution.
Curve B: Assay measured against a reference standard prepared by the standard addition method

addition technique was considered preferable. The same principle was adopted by Smith and Palmby[3] for the determination of lead in gasoline.

In the standard addition technique, the emission of the test solution is compared with the emission of an aliquot of the test solution to which a known amount of standard lead solution has been added. Because the concentration-transmittance curve was found to be linear, the unknown concentration of lead could be calculated from the relationship

$$\frac{x \,.\, (v_1 + v_2)}{v_1 x + v_2 y} = \%\mathrm{T} \,.\, 10^{-2} \qquad (2)$$

where

x = concentration of Pb in unknown solution,
y = concentration of Pb in added standard solution,
v_1 = volume of test solution aliquot,
v_2 = volume of standard added,
and $\%\mathrm{T}$ = observed transmittance reading.

Using this technique, an error in the observed transmittance reading is magnified by the calculations, and Curve B, Fig. 1 represents the error in the final result that may be introduced by a 1% error in the transmittance reading. From this curve, it can be seen that transmittance readings should preferably lie between 40% and 60% if the calculation errors are to be kept to a minimum. This corresponds to a minimum of 550 ppm and a maximum of 850 ppm of Pb in the test sample, using a check solution containing the suggested minimum content of 1400 ppm of Pb. These limits may be increased to higher values by using check solutions containing higher concentrations of lead but experience has indicated that the maximum concentration in the check solution should be limited to 2000 ppm of Pb. Above this limit the calibration curve began to deviate from a linear relationship, and precision was impaired because scale divisions corresponded to larger units of lead concentration.

The optimum conditions for the flame photometric determination of lead using the Hilger Flame Photometer appears to be the adjustment of the test solution so that it contains 700–1000 ppm of Pb and the adjustment of the check solution (by addition of standard lead solution) so that it contains approximately twice the concentration of lead in the test solution. The precision studies (*cf.* Table I) have confirmed the suitability of these limits.

Preparation of test solutions

One of the problems associated with solution of lead alloys is the ready hydrolysis of the salts of tin and antimony which are commonly found in association with the lead.

Elwell and Gidley[5] satisfactorily overcame this problem with copper-base alloys by dissolving the alloys in a mixture of nitric and hydrochloric acids.

In the present study, metals were retained in solution as citrate complexes following solution of the sample in concentrated sulphuric acid.

Several g of ammonium citrate were added to the sulphuric acid solution of the alloy and the acid was carefully neutralised with concentrated ammonia solution. During neutralisation, some cloudiness caused by lead sulphate appeared, but this largely disappeared on complete neutralisation of the acid. To ensure complete lead recovery and a perfectly clear solution for testing, the citrate solution was filtered through a fine sintered-glass crucible (P4), and the residue in the crucible was treated with hot ammonium acetate extraction solution. The filtrate was then diluted to a standard volume, so as to give a lead concentration of 700–1000 ppm.

With white metals containing a low concentration of lead, it was found advisable to isolate the lead initially as lead sulphate, and subsequently to dissolve it in hot ammonium acetate solution.

Check solutions were then prepared by carefully adding, with constant agitation, 0·15 to 0·20 ml of a standard lead solution (0·1000 g of Pb per ml) from an Agla Micro Syringe to a 20-ml aliquot of the test solution. Under these conditions, each addition of 0·10 ml gives an increase of approximately 500 ppm in the concentration of lead in the aliquot.

No detrimental effects from the presence of the citrates and acetates in the test solutions were observed in the subsequent flame photometric determinations. However, because of the poisonous nature of lead fumes, the flame attachment was housed in a fume chamber.

TABLE I.—PRECISION OF FLAME PHOTOMETER READINGS

Sample	No. of readings	Conc. of test soln., *ppm* of Pb	Conc. of "Check" soln. *ppm* of Pb	Precision* (Std. deviation, *ppm* of Pb)	
				Individual results	Mean of 3 readings
Lead nitrate solutions	15	1040	2080	±71	±26
	15	520	2080	±57	±33
	15	260	2080	±56	±22
	15	520	1040	±95	±78
Solder A, 43% Pb	15	860	1360	±51	±42
	18	860	1860	±43	±23
	15	860	2360	±62	±51
Solder B, 60% Pb	25	1200	1700	±111	±72
	25	1200	2200	±120	±103
	20	1200	2700	±130	±72
	42	900	1900	±79	±28
White metal A, 3·9% Pb	54	780	1780	±69	±35
White metal B, 84·5% Pb	27	850	1700	±43	±10

* The standard deviation was calculated from the formula $m = \sqrt{\Sigma x^2/n - 1}$ where x is the deviation from the mean and n the number of readings taken.

Precision of instrument readings

The errors associated with the analysis of lead in alloys can be broadly divided into two groups, namely, those associated with the dissolution of the sample, preparation of test solution, addition of standard solution, *etc.*, and those associated with instrumental variables such as flame fluctuations, atomising rates, *etc.*

The magnitude of the former group can be assessed from a study of the accuracy and reproducibility obtained in the analysis of a series of alloys. These results are discussed in the next section.

The magnitude of the error associated with instrumental variables can be assessed from a study of the precision of a series of readings on the same sample.

Multiple transmittance readings were therefore made using standard solutions of lead nitrate in water and using test solutions prepared from lead alloys. The precision of the readings was then calculated in terms of the standard or root mean square deviation using the formula

$$\text{Standard Deviation, } m = \sqrt{\Sigma x^2/n - 1} \qquad (3)$$

where x is the deviation from the mean reading and n the number of readings.

For comparison purposes the mean of every three readings was calculated, and the precision of these means was then determined.

The results of the precision calculations are summarised in Table I.

A number of deductions may be made from this Table. First, the worst precision was obtained with samples whose concentrations varied from the optimum limits previously suggested. For example, the test solution of Solder B, which contained 1200 ppm of Pb, gave poorer precision than the same sample prepared so as to have a lead concentration of 900 ppm. Similarly, poorer precision was obtained with lead nitrate solutions when a "check" solution containing only 1040 ppm of Pb was used.

Secondly, precision is greatly improved by considering only the mean of each three readings, which emphasises that multiple readings should be taken with every test solution.

Thirdly, the magnitude of the standard deviations emphasises the large errors that may be introduced in the final evaluation stage of analysis. Taking a single reading, the average standard deviation indicates the possibility of errors of the order of $\pm 10\%$ in the calculated lead content of the sample. On the other hand, using the mean of three readings and considering only those samples which satisfy the concentration limits previously suggested, a precision of ± 3–5% of total content may be predicted.

Using similar Hilger equipment together with a photo-multiplier attachment and the atomic absorption technique, Elwell and Gidley[5] obtained a precision (*i.e.*, standard deviation) of $\pm 0{\cdot}06\%$ for copper-base alloys containing 2·5 to 4% of lead. Thus the precision of the atomic absorption technique for the analysis of lead would appear to be at least twice as good as that obtainable by direct flame emission measurements.

Accuracy and reproducibility

Multiple samples of a number of alloys containing a certified lead content were analysed using the flame photometric method. The lead content of each sample analysed was obtained by substituting the mean of at least six transmittance readings in equation (2). The results obtained with these individual samples have been used to calculate the reproducibility of the sample preparation and final evaluation. This reproducibility (expressed in terms of a standard deviation) is summarised in Table II. It can be seen from this Table that the lead determinations were reproducible to within 4–6% of the total lead content.

The lead content of each alloy was finally calculated by averaging the results obtained with three samples of the alloy. The results thus obtained for the alloys are summarised in Table III and it can be seen from this Table that an accuracy of about $\pm 5\%$ of the total lead content was achieved. The composition of the alloys used is given in Table IV.

In order to improve the poor precision obtained with individual instrument readings (*cf.* Table I), a number of readings had to be taken for each sample.

TABLE II.—REPRODUCIBILITY OF LEAD ANALYSES

Sample	No. of assays	Mean Pb content, %	Max. dev. from mean	Standard deviation, %	Std. dev. as % of Pb content
Solder A	9	40·9	4·1	±2·5	6·2
Solder B	12	60·1	5·3	±3·8	6·3
White metal A	4	3·63	0·21	±0·15	4·2
White metal B	3	84·5	4·0	±3·7	4·3

This need for multiple readings has been noted by workers using the flame photometric method for the determination of lead in gasoline. Smith and Palmby[3] used the standard addition method for calibration, and the lead determinations were found to be accurate to about 2% of the amount of lead present in the gasoline. This higher degree of accuracy in comparison with the values quoted in Table III may be attributed in part to the tenfold increase in emission sensitivity obtained by burning gasoline samples, in part to the use of a photo-multiplier in the detection unit, and in part to the use of an atomiser-burner.

Using the atomic absorption technique for the estimation of lead, a reproducibility of the order of 2% and an accuracy (expressed as standard deviation) of 0·025% on samples containing 2·5 to 4% lead was obtained.[5] This again demonstrates the superiority of the atomic absorption technique over direct emission studies. However, the results obtainable using the normal flame photometric technique are sufficiently accurate for routine testing and even with multiple readings the method is faster than conventional gravimetric or titrimetric procedures.

Method for the analysis of solder

Transfer weighed samples of solder containing 0·0700–0·1000 g of lead to 250-ml Erlenmeyer flasks and add 5–10 ml of concentrated sulphuric acid. Cover with a watch glass, and heat to dissolve

TABLE III.—ACCURACY OF LEAD ANALYSES

Sample	Determined Pb content, %	True Pb content, %	Error % Pb	Error as % of lead content
Solder A	39·9	43·0	−3·1	7·2
	41·4		−1·6	3·7
	41·3		−1·7	4·0
Solder B	62·7	60·1	+2·6	4·3
	57·0		−3·1	5·2
	60·0		−0·1	0·1
	60·7		+0·6	1·0
White metal A	3·63	3·90	−0·27	7·4
White metal B	84·5	84·5	0·0	0·0
			Standard Deviation ±4·7%	

TABLE IV.—COMPOSITION OF ALLOYS USED

Solder A	43·0% Pb, 56·9% Sn.
Solder B	60·1% Pb, 39·6% Sn.
White Metal A	3·90% Pb, 84·0% Sn, 7·50% Sb, 4·10% Cu.
White Metal B	84·5% Pb, 5·09% Sn, 10·4% Sb.

the alloy. Cool slightly, dilute with 10 ml of water, and add 5 ml of 50% ammonium citrate solution. From a pipette carefully add 15*N* ammonia solution down the sides of the flask (with constant swirling) to neutralise the acid (Note 1). Heat the solution on a hot plate for a few min. Decant the solution through a fine sintered-glass crucible (P4), using slight suction. Collect the filtrate.

Add 10 ml of boiling ammonium acetate extraction solution (Note 2) to the flask, heat to dissolve any residue of $PbSO_4$, and filter the contents of the flask through the same glass crucible. If any residue remains in the flask or crucible, repeat the extraction with a further 5 ml of the ammonium acetate solution. Wash the crucible with water. Combine all filtrates and transfer to a 100-ml standard flask, diluting to the mark with water. This is the "test" solution.

Take a 20-ml aliquot of this test solution, and from an Agla Micro Syringe carefully add 0·15–0·20 ml of standard lead solution (Note 3). This is the "standard" solution.

Set the wavelength drum of the flame photometer to 405·8 mμ, and adjust the zero control while spraying distilled water into the flame. Adjust the instrument to give 100% transmittance on the introduction of the "standard" solution. Measure the transmittance of the "test" solution.

Take the mean of a series (Note 4) of transmittance readings. Calculate the percentage of lead in the original alloy by substitution in the equation

$$\% \text{ Lead} = \frac{\alpha \,.\, v_1 \,.\, 10^{-4} \,.\, v_3 \,.\, c}{[(1 - \alpha) \,.\, v_2 + v_3] \,.\, w}$$

where

α = % transmittance of sample $\times 10^{-2}$.
v_1 = Volume of test solution after dilution (*e.g.* 100 ml)
v_2 = Volume of aliquot used for "check" solution.
v_3 = Volume of standard lead solution added.
c = Concentration of standard lead solution (ppm).
w = Weight of alloy taken (g).

Notes

1. Most of the precipitate present in the early stages disappears when neutralisation is complete.

2. The ammonium acetate extraction solution is prepared by diluting a saturated solution of ammonium acetate with twice its volume of distilled water and adding 30 ml of 80% acetic acid to each litre of solution.[7]

3. A suitable standard lead solution may be prepared by dissolving 15·9850 g of AnalaR $Pb(NO_3)_2$ in 100 ml distilled water. This is equivalent to 10^5 ppm of Pb or 0·1000 g of Pb per ml.

4. A minimum of six readings is recommended.

Although this method has been developed for the analysis of solder, only minor modification is required to permit its application to other forms of alloys containing lead.

If the lead content of any type of alloy be first isolated as lead sulphate, then solution of this precipitate in ammonium acetate provides the required "test" solution and the analysis can be completed as already described. The presence of some ammonium citrate in the acetate extraction mixture ensures solution of any co-precipitated metal ions. This approach was tested with two white metal samples, containing 3·9 and 84·5% of Pb respectively, and it can be observed from Tables II and III that the reproducibility and accuracy achieved was slightly better than that obtained in the solder analysis. This improvement coincides with improved precision in the individual measurements. Because of the lower concentration of salts in the solution, the rate of atomisation was similar to that of lead nitrate solutions and the precision obtained was of the same order (*cf.* Table I).

Method for the analysis of white metal

Transfer weighed samples of white metal containing 0·0700–0·1000 g of lead to 250-ml Erlenmeyer flasks, add 10 ml of conc. sulphuric acid and cover with a watch glass. Heat till the sample is dissolved and the residue is white. Cool (but not below 60°), dilute carefully with 50 ml of water, and heat to boiling until the precipitate settles quickly on the removal of heat. Maintain above 60° until the precipitate settles completely. Decant solution through a fine sintered-glass crucible (P4). Retain most of the precipitate in the flask and discard the filtrate.

Add 5 ml of 50% ammonium citrate and 5 ml of boiling ammonium acetate extraction mixture to the flask. Heat to dissolve the precipitate. Filter the contents of the flask through the same glass crucible and collect the filtrate.

Extract the contents of the flask once more with 5 ml of boiling ammonium acetate extraction mixture. Collect the filtrate and wash the flask and crucible with water. Combine all the filtrates and make up to volume with water to provide the "test" solution. Complete the determination as in the solder method.

DISCUSSION

One of the main attributes of flame photometry is the relative speed with which analyses can be performed when compared with other standard techniques. Often the penalty paid for the increased speed is a loss in accuracy.

The flame photometric determination of lead possibly provides the extreme case, since the excitation of lead salts by an oxygen-fuel flame results in lines of very low intensity. However, it has been shown in this study that satisfactory analysis can still be performed if suitable limits of lead concentration are chosen and multiple readings are made. The lead determinations were reproducible to $\pm 5\%$ of the total lead content, and the accuracy of the determinations was of the same order.

It is emphasised that the results obtained in this study represent the accuracy and precision that may be obtained using the standard instrument. Improved results can be obtained by using a photo-multiplier attachment,[3,5] and the advantages of the atomic absorption technique have been clearly demonstrated.[5,6]

An alternative approach to improved accuracy and precision is that recommended by Dean,[8] who suggests the extraction of lead into organic solvents and direct aspiration of the organic phase into the flame. The enhancement of emission sensitivity caused by the organic phase has been clearly demonstrated with gasoline, but for safety reasons organic solvents should only be used with flame photometers fitted with an integral type of burner-atomiser. The Hilger attachment is fitted with a separate glass atomising chamber. As a consequence the beneficial effect of organic solvents could not be investigated in this study because of the danger of explosion within the chamber.

Acknowledgements—Two of us (C. L. C. and W. F. P.) wish to thank The Queen's University of Belfast for the research fellowships which enabled us to undertake this research. One of us (W. F. P.) also wishes to thank the University of New South Wales for granting study leave.

Zusammenfassung—Methoden zu flammphotometrischen Analyse von Bleilegierungen werden beschrieben. Die untersuchten Proben enthielten 4–85% Blei. Reproduzierbarkeit und Genauigkeit der resultate war ±5% des Bleigehaltes.

Résumé—Les auteurs décrivent des méthodes d'analyse d'alliages de plomb par photométrie de flamme. Les échantillons analysés contenaient de 4 à 85% de plomb et les résultats obtenus étaient reproductibles à ±5% de la quantité de plomb présent. La précision des analyses était de ±5% de la teneur en plomb.

REFERENCES

[1] P. T. Gilbert, *Amer. Soc. Testing Materials*, Spec. Tech. Publ. 116, 1951, 77.
[2] M. Whisman and B. H. Eccleston, *Analyt. Chem.*, 1955, **27**, 1861.
[3] G. W. Smith and A. K. Palmby, *ibid.*, 1959, **31**, 1798.
[4] J. A. Dean, *Flame Photometry*. McGraw-Hill Book Co. Inc., New York and London, 1960. p. 238.
[5] W. T. Elwell and J. A. F. Gidley, *Analyt. Chim. Acta*, 1961, **24**, 71.
[6] J. W. Robinson, *ibid.*, 1961, **24**, 451.
[7] N. H. Furman, *Scott's Standard Methods of Chemical Analysis*. 5th Edition, D. Van Nostrand Co. Inc., New York, 1939. p 512.
[8] J. A. Dean, *Analyst*, 1960, **85**, 621.

Talanta, 1962, Vol. 9, pp. 153 to 167. Pergamon Press Ltd. Printed in Northern Ireland

CHELOMETRIC TITRATIONS WITH AMPEROMETRIC END-POINT DETECTION

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Summary—Anodic chelon waves may be used as indicator waves in the amperometric titration of metal ions which exhibit poorly defined reduction waves. By this method, also, mixtures of metal ions whose log K values differ by less than 4 units may be selectively titrated. Buffers and chelons may be selected to improve selectivity, and the procedure is more rapid than the usual amperometric methods. Results are given for selected ions and mixtures of ions. The interference of halide ions must be overcome.

THREE different methods have been proposed for amperometric titrations with ethylenediaminetetra-acetic acid, EDTA. The most obvious uses the decrease in reduction wave height of the uncomplexed metal ion during the course of the titration.[7] This method is applicable when the reduction waves of the free metal ion and the metal chelonate are sufficiently well separated, and where that of the free metal ion occurs at a reasonably accessible region of potential. Since such conditions do not always exist, some alternative methods are desired.

One is to add an *indicator ion*; this is a metal ion species which is reducible at some practical potential and which, under the solution conditions chosen, forms a weaker complex with the chelon than the metal ion to be determined. The amperometric titration of calcium, for example, was accomplished by addition of zinc ion (zincate ion under the solution conditions chosen); a decrease in the diffusion current of zincate ion commenced after calcium was complexed and served to mark the end point.[5]

A second alternative is based on the appearance of an *anodic wave for the free chelon* after the end-point.[6,10] This electrode reaction may be written:

$$Hg^0 + H_n Y^{n-4} \rightarrow Hg Y^{2-} + nH^+ + 2e^- \qquad (1)$$

This method offers several advantages which have made its further investigation profitable and interesting.

A significant advantage of this latter method arises from the fact that the titration may be performed at a potential where the reduction wave of oxygen does not interfere. Hence the time-consuming operation of removing oxygen from the solution before analysis and after the addition of each aliquot of titrant is eliminated. Also, metals with large negative reduction potentials, such as calcium or barium, may be titrated without the introduction of "indicator" ions into the solution. Metal ions which exhibit ill-defined reduction waves may also be analysed conveniently. Furthermore, metal ions, such as zinc, may be easily titrated in the presence of a more readily reducible species, such as nitroaniline. This method should be readily adaptable to the use of rotary mercury electrodes in cases where higher sensitivity is desired.

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The disadvantages of the proposed method include those common to amperometric analysis, with the exception of the oxygen interference mentioned above. The presence of halide ions interferes[10] and must be avoided.

SELECTION OF POTENTIALS FOR ANALYSIS

A principal operational difference between the anodic wave method and the other methods is, of course, the potential applied during the titration. In the first two methods, a potential at which one of the metals in the solution is reduced is applied. In the anodic method, the potential applied should correspond to a point on the diffusion plateau (anodic wave) for the chelon.

In order to select a suitable potential, it is expedient to consider polarograms which illustrate the various factors affecting the limits of the chelon wave (see Fig. 1). Either the initiation of the oxygen reduction wave, *a*, *or* the onset of the chelon wave (where mercury is anodically oxidised), *b*, establishes the negative limit of useful potentials. The less negative of the two values determines this limit and is designated as E_{min}. The positive limit of the potential is always controlled by the buffer present in solution and is denoted as E_{max}. Hence, the potential region useful for analysis, ΔE, is dependent on the buffer type and concentration and on *either* the oxygen wave *or* the chelon wave. Consequently, each of these factors was investigated.

Oxygen wave

The oxygen wave is difficult to characterise in a definitive manner because a number of different features determine its reduction potential. Kern[4] dismisses the special effects of pH and buffer components as adsorption effects, and takes the electron transfer step as the rate-determining step. In this study, the potential value at which the oxygen wave begins was found to vary from 0·05 V *vs.* S.C.E. at pH 1 to 0·10 V at pH 10·9; this is in agreement with the results found by Kern.

To determine practical limiting values of E_{max} and E_{min}, a suitable current level was first established. For this purpose, consider the practical titration where one drop (0·05 ml) of chelon in excess of the equivalence point is added to 50 ml of solution; the current given by this concentration of free chelon may be calculated using the Ilkovič equation and known diffusion coefficients. The resultant current will be 0·40 μA for the chelon hydroxyethyl-ethylenediaminetriacetic acid (HEDTA), and 0·48 μA for diethylenetriaminepenta-acetic acid (DTPA). The values given in Table I were obtained by taking the experimentally observed EMF corresponding to a current of 0·4 μA in various buffers. Although the concentration of chelon used here is somewhat arbitrary, it nevertheless represents a practical choice applicable to the titration of approximately 0·25 mmoles of metal in a 50-ml volume.

Buffer wave

The maximum potential that may be applied in the absence of a buffer depends on the formation of mercury^{I} ions or mercury^{II} oxides. Because of the necessity of having a buffer present, the limit is less, since the buffers complex with the mercury^{II} to some extent. Consequently the type and concentration of buffer establishes the maximum potential limit for an anodic wave titration.

The effect of buffers on potentiometric chelometric titrations using the mercury electrode was studied by Reilley and Schmid.[9] The upper potential limit, corresponding

TABLE I.—EFFECTS OF BUFFERS ON LIMITING POTENTIALS

Buffer	pH	Conc., *molar*	E_{max}	E_{min}	ΔE
HNO_3	1·0	0·10	0·290	0·050	0·260
Hexamethylenetetramine	4·62	0·10	0·285	0·042	0·243
		0·075	0·290	0·042	0·248
		0·05	0·301	0·040	0·261
		0·025	0·330	0·030	0·300
Acetate	4·7	0·10	0·290	0·050	0·240
Potassium acid phosphate	5·5	0·10	0·220		0·190
Triethanolamine	7·8	0·10	0·108	0·025	0·083
		0·075	0·118	0·025	0·095
		0·05	0·120	0·025	0·095
		0·10	0·160	0·046	0·114
Trishydroxymethylaminomethane	7·91	0·10	0·095	0·039	0·056
		0·075	0 102	0·032	0·070
		0·05	0·110	0·035	0·075
		0·01	0·150	0·049	0·101
Diethanolamine	8·8	0·10	0·084	0·002	0·082
		0·05	0·096	0·007	0·091
		0·01	0·125	0·016	0·109
Ammonia	9·3	0·10	0·042	−0·007	0·049
		0·075	0·048	−0·008	0·056
		0·050	0·057	−0·005	0·062
		0·025	0·062	−0·007	0·094
2-aminoethanol	9·5	0·10	0·030	−0·027	0·057
		0·05	0 052	−0·025	0·077
		0·025	0·064	−0·023	0·087
		0 01	0 080	−0·025	0·105
3-aminopropanol	10·0	0·10	0·028	−0·050	0·078
		0·05	0·040	−0·050	0·090
		0·025	0·053	−0·050	0·103
Diethylamine	10·9	0·10	0·007	−0·102	0·109
		0·05	0·013	−0·096	0·109

to E_{max}, was discussed, and was shown, as expected, to be largely dependent on the stability of the mercury^{II} buffer complex.

The existence of mixed complexes containing mercury, buffer (B), and chelon (Y) was also considered. Mercury^{II}-EDTA forms a complex of the type $HgBY$ with most *nitrogen*-containing buffers. On the other hand, chelons like ethyleneglycol bis-(β-aminoethyl ether)-*N*,*N*′-tetra-acetic acid (EGTA), and diethylenetriamine-penta-acetic acid (DTPA) have little tendency to form such complexes. In contrast,

oxygen type buffers, such as acetate and phthalate, do not form stable mixed complexes with mercury^{II}-EDTA. When a complex of the type HgBY is formed, the minimum potential limit imposed by the onset of the chelon wave is shifted favourably to more negative values. On the other hand, this imposes a further complication when stability constants are measured polarographically, in that another equilibrium must be considered in interpreting the half-wave potentials.

The positive potential limit may be decreased by the formation of insoluble mercury^{I} halides in solutions which have high halide concentrations. Consequently, care should be taken that the titration solution be kept relatively free of halide ions.

In view of the above, the ideal buffer should form a relatively weak complex with mercury. Taking this into consideration, only buffers which gave a ΔE value greater than 0·08 V were used, with the exception of ammonia, where ΔE is 0·049 V (see Table I). The use of ammonia necessitates a more careful control of both pH and applied potential.

In an actual analysis, each sample is neutralised to a pH near 7 *before* the addition of buffer; this permits use of a minimum quantity of buffer consistent with ample buffer capacity.

Chelon wave

Fig. 1 shows that either the chelon wave or the initiation of the oxygen wave may establish the negative potential limit. Since only the diffusion plateau of the chelon

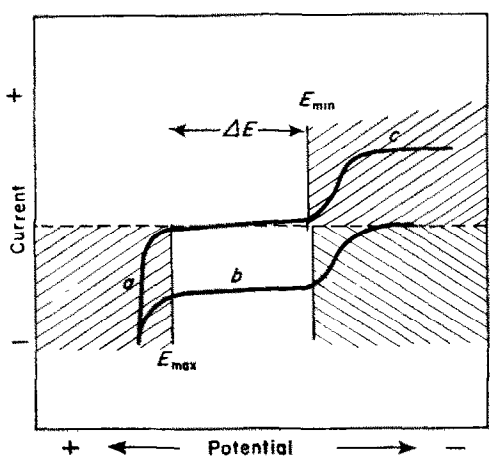


FIG. 1.—Polarographic waves affecting choice of potential.
A. Anodic oxidation of mercury in the presence of a buffer.
B. Anodic oxidation of mercury in the presence of a chelon.
C. Cathode reduction of oxygen.

wave is truly useful for analytical purposes, the potential where the current departs from this plateau is taken as the limiting potential.

Polarographic and potentiometric studies indicate the properties which one can expect for a given chelon in a practical titration. Fig. 2 represents the results of the investigation of a typical chelon, *N*-hydroxyethylethylenediaminetriacetic acid, HEDTA. Line *b* is the anodic oxidation of mercury in the presence of free chelon,

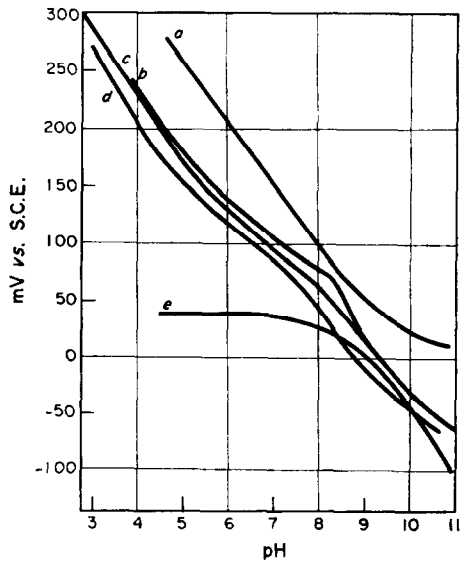


FIG. 2.—HEDTA polarographic and potentiometric waves.
A. E_{max} *vs.* pH
B. Anodic oxidation of mercury in $1{\cdot}342 \times 10^{-3}M$ HEDTA.
C. Potentiometric-pH study of equimolar mixture of Hg-HEDTA and HEDTA, ($1{\cdot}342 \times 10^{-3}M$).

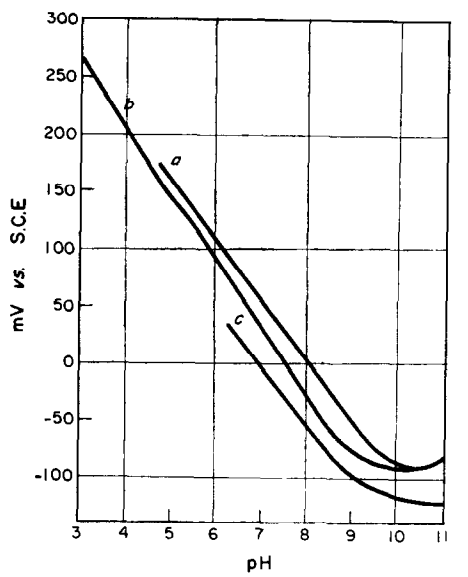


FIG. 3.—EGTA polarographic and potentiometric waves.
A. Anodic oxidation of mercury in $0{\cdot}972 \times 10^{-3}M$ EGTA.
B. Potential-pH curve of equimolar Hg-EGTA and EGTA, both $0{\cdot}972 \times 10^{-3}M$.
C. Cathodic reduction of $0{\cdot}972 \times 10^{-3}M$ Hg-EGTA.

and line *d* is the cathodic reduction of the mercury^{II}-chelonate, the e.m.f. shown being the polarographic half-wave potentials. Line *c* is the potentiometric-pH relationships of an equimolar mixture of mercury^{II}-chelonate and free chelon. This line should coincide with the $E_{\frac{1}{2}}$-pH line of a solution of the same composition if the diffusion coefficients of the mercury^{II}-chelonate and free chelon are identical. However, even when corrections are made for diffusion-coefficient differences (which actually are small), coincidence is still not observed because of the degree of overall irreversibility of the electrode reactions. In fact, the separation of the anodic and cathodic lines (see Figs. 2, 3, and 4) serve as an indication of this, the more widely separated being the more irreversible. Thus, it may be seen that, while DTPA and

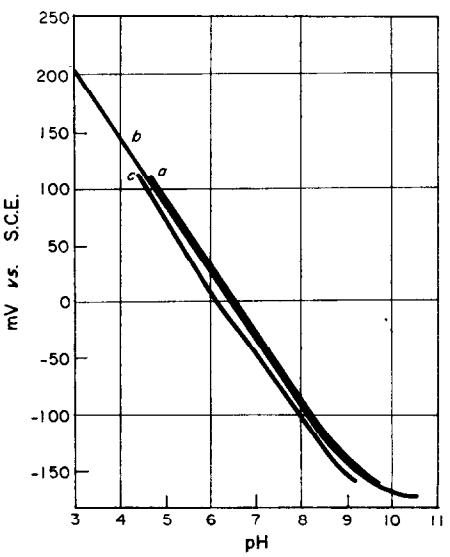


FIG. 4. —DTPA polarographic and potentiometric waves.
A. Anodic oxidation of mercury in $1{\cdot}088 \times 10^{-3}M$ DTPA.
B. Potential-pH curve of equimolar Hg-DTPA and DTPA, both $1{\cdot}088 \times 10^{-3}M$.
C. Cathodic reduction of Hg-DTPA, $1{\cdot}088 \times 10^{-3}M$.

HEDTA undergo fairly reversible reactions, EDTA is much less reversible. (Corrections for IR drop in the polarographic system were found to be insignificant.)

From polarographic and potentiometric data, the stability constants of the mercury^{II}-chelonates were calculated. The method of Goffert, Michel, and Duyckaerts[1] was used to calculate the stability constants from polarographic data, while the method of Schmid and Reilley[11] was used with the potentiometric data. Table II lists the calculated values and values previously reportedin the literature.

SELECTION OF TITRATION CONDITIONS

The metal ion or mixture of metal ions to be analysed ultimately determines the conditions necessary for a successful analysis. Principles which govern the selection of an appropriate pH in any chelometric analysis are valid here, and the pH effect, *i.e.* the change of pH for selective titrations of the components of a mixture, can be employed to advantage. However, a corresponding change in applied potential

TABLE II. MERCURY CHELONATE STABILITY CONSTANTS

Chelon	log K, calculated	Method of determination	log K, literature	Reference	log K^{H}_{HMy}
HEDTA	20·1	potentiometric	20·1	2	8·37
DTPA	27·0	potentiometric	27·0	2	11·79
	27·2	polarographic			
EDTA	23·9	potentiometric	23·8	11	11·95
	23·9	polarographic			
CyDTA	23·7	potentiometric	24·3	12	10·32

is necessary for an effective analysis of mixtures. Fig. 5 illustrates the results of such a titration for a mixture of copper and nickel with triethylenetetramine, trien. As shown above, the potential range suitable for the analysis is governed by the buffer and the chelon.

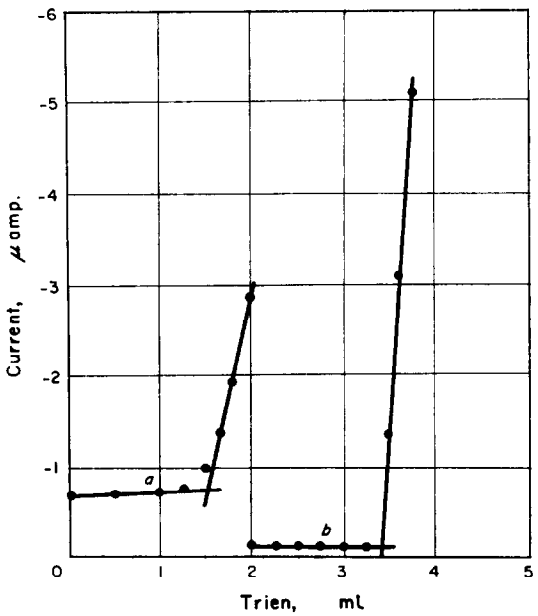


FIG. 5.—Titration of a Cu-Ni mixture with trien.
A. Titration of Cu^{2+} in phthalate buffer at a pH of 5·5.
B. Titration of Ni^{2+} in ammonia buffer at pH 9·3.

Selective titrations can sometimes be effected by the use of two different chelons, often with no change in pH. This method has more stringent thermodynamic and kinetic limitations, however. This may be illustrated by the titration of a mixture of zinc and calcium. These components in a single aliquot may be selectively analysed in ammonia buffer by first titrating zinc with trien and then titrating calcium with EDTA. Thermodynamic considerations require that the effective stability constant of calcium-trien be so low that essentially no calcium will complex with trien after the zinc end-point is reached. In addition, the exchange shown by reaction 2 must not proceed in the forward direction.

$$\text{Zn-trien} + \text{Ca-EDTA} \rightleftharpoons \text{Zn-EDTA} + \text{trien} + Ca^{++} \qquad (2)$$

When such conditions are met, the metal components are easily titrated selectively. Fig. 6 represents a combination of this method with the pH effect. Table III shows the results of this analysis.

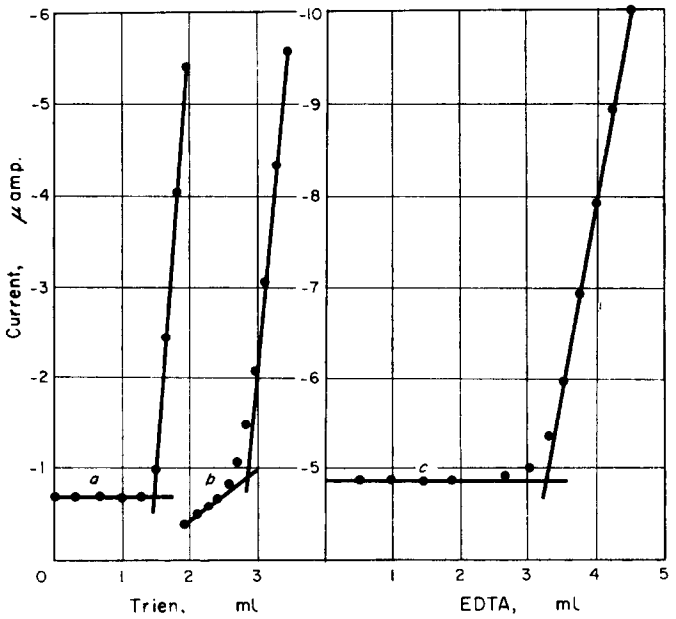


FIG. 6.—Titration of a Cu-Ni-Ca mixture.
A. Titration of Cu^{2+} in phosphate buffer at a pH of 5·5 with trien.
B. Titration of Ni^{2+} ammonia buffer at a pH of 9·3 with trien.
C. Titration of Ca^{2+} ammonia buffer at pH 9·3 with EDTA.

Fig. 7 illustrates typical curves obtained for several titrations of this type. A nickel-magnesium analysis (Fig. 7a) is not feasible since the effective log K value for nickel-EDTA is nearly 10 units greater than the value for magnesium-EDTA. Consequently, reaction 2 would take place in the forward direction to a large extent and there would be little, if any, magnesium-EDTA formed. The EDTA added beyond the nickel-trien end-point would simply replace the trien from the nickel-trien chelonate.

The analysis of a zinc-magnesium mixture by this method is also impossible. However, Fig. 7b shows a trend that can be interpreted as the occurrence of a reaction similar to reaction 2, but to a smaller extent than in the case of the nickel-magnesium mixture.

In the case of the nickel-calcium mixture in Fig. 7c, the titration curve appears useful. Nevertheless, the experimental results indicate that the second end-point occurs too soon. Obviously some of the EDTA added during the titration reacts with the nickel-trien.

The zinc-calcium mixture represented by Fig. 7d fulfils the thermodynamic and kinetic requirements, and may be successfully titrated by this method. Table III gives the results of this titration.

EXPERIMENTAL

Apparatus

Instruments: All polarographic and amperometric studies were made with a Leeds and Northrup

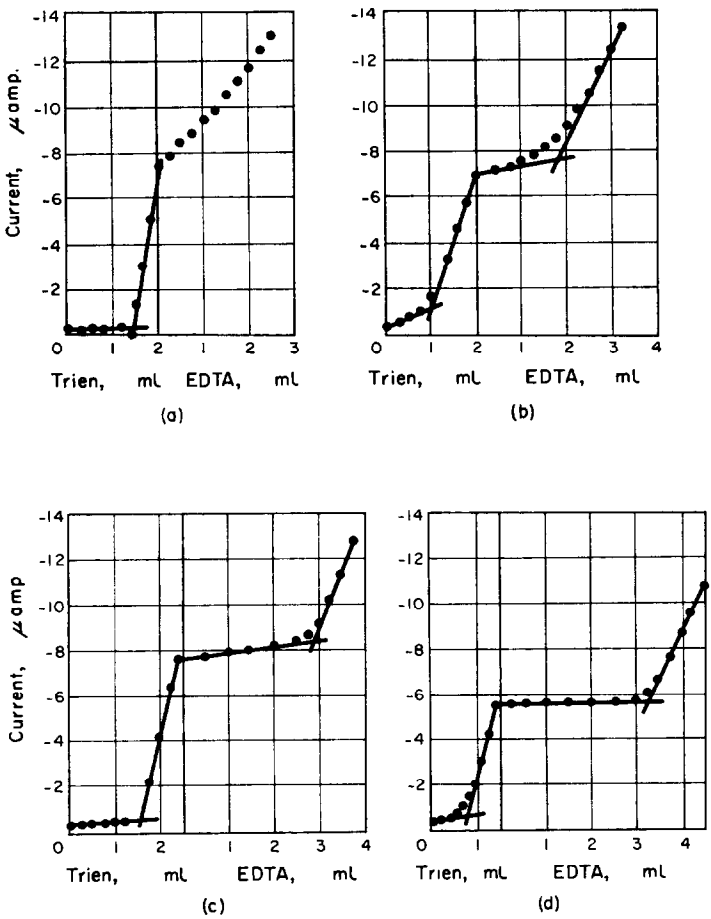


FIG. 7.—Selective titrations with *no* pH change.

A. Titration of Ni-Mg mixture in ammonia buffer at pH 9·3 with trien and EDTA.
B. Titration of Zn-Mg mixture in ammonia buffer at pH 9·3 with trien and EDTA.
C. Titration of Ni-Ca mixture in ammonia at pH 9·3 with trien and EDTA.
D. Titration of a Zn-Ca mixture in ammonia at pH 9·3 with trien and EDTA.

Electrochemograph. A Leeds and Northrup pH indicator Type 7764 was used for pH measurements. Potential measurements were made with a Rubicon portable precision potentiometer, type 2730.

Electrodes: A saturated calomel electrode and a dropping mercury electrode were used for all polarographic and amperometric work. During titrations and during some polarographic runs a shield was used for the dropping mercury electrode to eliminate adverse stirring effects. Fig. 8 shows the shield fitted with a rubber bulb of the medicine-dropper type, which is repeatedly squeezed after the addition of each aliquot of titrant to ensure homogeneity of solution inside and outside the shield. Only a few seconds are necessary before the solution within the shield is sufficiently quiet for the current to be diffusion-controlled. With this device, stirring throughout the titration is possible without adverse effects, and the time required for an analysis is greatly reduced. (In performing other amperometric titrations where oxygen interferes and must be removed from the solution, bubbling with nitrogen may proceed throughout the titration so long as the bubbles do not enter the shield.)

A gold amalgam electrode was used for the potentiometric studies. Because halide ions interfere with the potentiometric results, the interior of the saturated calomel electrode (Leeds and Northrup

TABLE III. RESULTS OF TITRATIONS OF MIXTURES OF METAL IONS

Mixture	Metal titrated	Present, *mg*	Found, *mg*	Error, %
Ni + Cd	Cd	29·42	29·48	0·2
			29·55	0·4
			29·10	1·1
	Ni	18·66	18·92	1·4
			18·99	1·8
			18·99	1·8
Cu + Ni	Cu	15·91	15·71	1·2
			15·81	0·6
			15·97	0·4
	Ni	18·66	18·53	0·7
			18·53	0·7
			18·44	1·2
Ca + Zn + Cu	Cu	15·91	15·66	1·6
			15·50	2·6
			15·61	1·9
	Zn	14·47	14·48	0·1
			14·75	1·9
			14·53	0·4
	Ca	13·34	13·07	2·0
			13·07	2·0
			13·11	1·7
Ni + Zn	Ni	14·93	14·85	0·5
			14·93	0·0
			14·93	0·0
	Zn	11·76	11·77	0·1
			11·77	0·1
			11·80	0·3
Cu + Zn + Ca	Cu	15·91	15·66	1·6
			15·50	2·6
			15·61	1·9
	Zn	14·47	14·48	0·1
			14·75	1·9
			14·53	0·4
	Ca	13·34	13·07	2·0
			13·07	2·0
			13·11	1·5

1199–31 reference electrode) was coated with a thin layer of agar-agar gel saturated with KNO_3. This effectively prevented the diffusion of chloride ions from the electrode into the reaction vessel. This type of reference electrode was also used in the bismuth titration, since formation of BiOCl would otherwise result.

Titrants

Approximately 0·1*M* solutions were prepared from the salts and standardised against a standard copper nitrate solution. The latter was prepared by dissolving a weighed portion of electrolytic copper in nitric acid and diluting to an appropriate volume.

Ethylenediaminetetra-acetic acid, EDTA: A 0·1*M* solution was prepared by dissolving an appropriate amount of the disodium salt in water. It was standardised in acetate buffer at a pH of 4·6 with the standard copper solution, using SNAZOXS[18] as an indicator.

Hydroxyethylethylenediaminetriacetic acid, HEDTA: Standardised in ammonia buffer at a pH of 8·0 with murexide as the indicator, using the standard copper solution. It is marketed as Chel DM Acid by Geigy Industrial Chemicals.

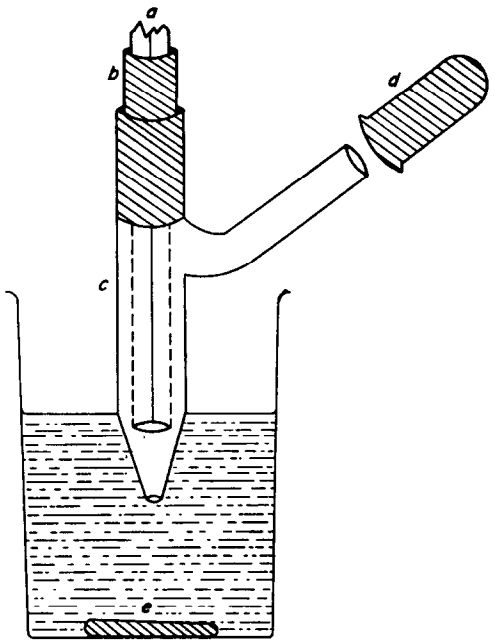


FIG. 8.—Amperometric titration assembly.
A. Dropping mercury electrode.
B. Gasket of rubber tubing.
C. Electrode shield.
D. Dropper bulb.
E. Stirrer magnet.

Diethylenetriaminepenta-acetic acid, DTPA (Geigy Industrial Chemicals): Standardised with the standard copper solution at a pH of 4·5 in acetate buffer, using SNAZOXS[18] as an indicator.

Ethyleleglycol bis-(β-aminoethylether)-N,N′,*tetra-acetic acid, EGTA*, (Geigy Industrial Chemicals): Standardised potentiometrically in ammonia buffer with the standard copper solution at a pH of 8·5.

Triethylenetetramine, trien: Purified according to the method of Reilley and Holloway.[8] Standardised potentiometrically at a pH of 10 in ammonia buffer using the standard copper solution.

Tetraethylenepentamine, tetren: Standardised with copper potentiometrically in potassium acid phthalate buffer at a pH of 5·8. It was purified according to the method of Reilley and Holloway.[8] Both trien and tetren (technical grade) were obtained from Carbide and Carbon Chemical Company. A purified grade of trien disulphate is available from J. T. Baker Chemical Company.

Metal ions

Standard copper nitrate solution: Made by dissolving a weighed portion of electrolytic copper metal in nitric acid. The solution was heated gently to expel oxides of nitrogen and some excess acid, transferred to a volumetric flask, and diluted to an appropriate volume. Before weighing, the copper was cleaned with 1:3 nitric acid, washed with distilled water and then with ethanol, and dried at 85°.

Mercury^{II} *nitrate solution:* Prepared in essentially the same manner as the copper nitrate solution. A weighed portion of the pure metal was dissolved in nitric acid and the solution was heated gently to expel oxides of nitrogen and some excess acid. This solution was standardised potentiometrically in pyridine buffer with EDTA.

All other metal solutions were made by dissolving approximately 0·1 mole of the nitrate salt in 1 litre of water.

Calcium nitrate: Standardised in diethylamine buffer at a pH of 12·2 with Calcon (C.I. 15705) as the indicator, using EDTA as the titrant.

Zinc, cadmium and magnesium solutions: Standardised in ammonia at a pH of 10·0 with EDTA using Eriochrome Black T (C.I. 14645) as the indicator. Nickel was standardised similarly using murexide as the indicator.

Bismuth^{III} nitrate solution: Made by dissolving 0·1 mole of the salt in a litre of 0·1*N* nitric acid This solution was standardised at a pH of 1 with SNAZOXS[18] as an indicator, using EDTA.

Lead nitrate solution: Standardised with EDTA at a pH of 5 in acetate buffer, using Xylenol Orange as the indicator.

Barium nitrate solution: Standardised at pH 12 in ammonia and NaOH with Eriochrome Black T (C.I. 14645) as the indicator, using EDTA as titrant.

Buffer solution

All buffer solutions were made by dissolving approximately 1 mole of the acid or base in 1 litre of water. Each solution was then half neutralised with concentrated HNO_3 or carbonate-free 50% NaOH. A pH meter was used to locate conveniently the exact half-neutralisation point where pH = pK. The buffer was added to each sample before analysis in an amount sufficient to give a concentration of 0·1*M* during the analysis.

PROCEDURES AND RESULTS

The titrations were performed in a 150-ml beaker equipped with a magnetic stirrer as shown in Fig. 8. The stirrer could not be mounted on the same ring stand as the electrodes, since vibrations from the motor affected the formation of the mercury drop. Also, the beaker did not rest directly on the stirrer, but was held approximately 1 mm above it. This eliminated any effect which the vibration might have had on diffusion of species to the electrode surface. These precautions were necessary since the solution was stirred at all times during the analysis.

Titrations of individual metal ions

To test the feasibility of the proposed method, all metal ions were titrated individually before any mixtures were titrated. The results of these titrations are given in Table IV. In each case the buffer concentration was 0·1*M* and the supporting electrolyte was 0·1*M* KNO_3; no maximum suppressor was found to be necessary. A 10-ml burette was used to deliver the titrant, and a single titration takes about 15 min.

Calcium, magnesium, and zinc: To a sample containing approximately 0·25 mmoles of calcium, magnesium, or zinc ions add 7·5 ml of 1*M* ammonia buffer and dilute the solution to 75 ml with 0·1*N* KNO_3. Adjust the pH to 9·3 and perform the titration at 0·002 V applied potential *vs.* S.C.E. in each case. EDTA is used to titrate calcium and magnesium, while trien is used for zinc.

Cadmium, nickel: To a sample which contains approximately 0·25 mmoles of cadmium or nickel add 7·5 ml of 1*M* hexamethylenetetramine buffer, dilute the solution to 75 ml with 0·1*N* KNO_3, and adjust the pH to 4·6. Titrate with HEDTA at an applied potential of 0·28 V *vs.* S.C.E.

Copper: To a sample of approximately 0·25 mmoles of copper ions, add 14 ml of 0·5*M* potassium acid phthalate buffer and dilute to 75 ml with 0·1*N* KNO_3. Adjust the pH to 5·5 and titrate with trien at an applied potential of 0·25 V *vs.* S.C.E.

Lead: To a sample containing approximately 0·25 mmoles of metal ion, add 7·5 ml of 1*M* acetate buffer and dilute to 75 ml with 0·1*N* KNO_3. Titrate lead with EDTA at a pH of 4·7 and a potential of −0·03 V *vs.* S.C.E.

Bismuth: To a sample containing approximately 0·25 mmoles of bismuth in 0·1*N* HNO_3, add sufficient 0·1*N* KNO_3 to dilute the volume to 75 ml, and adjust the pH to 1·5 with HNO_3. Titrate with DTPA at an applied potential of 0·36 V *vs.* S.C.E. BiOCl has a tendency to precipitate when chloride ions are present, so the calomel cell used a reference electrode should be treated as described above to prevent diffusion of chloride ions into the solution.

Titrations of mixtures of metal ions

Nickel and cadmium: To a solution containing approximately 0·25 mmoles of each metal ion, add 7·5 ml of 1*M* hexamethylenetetramine buffer and dilute to 75 ml with 0·1*N* KNO_3. Adjust the pH to 4·0 and titrate with HEDTA at an applied potential of 0·32 V *vs.* S.C.E. The pH drops about 0·5 unit during the titration, which enhances the separation. Add NaOH to bring the pH to 4·6, and titrate cadmium with HEDTA at the same potential.

TABLE IV. RESULTS OF INDIVIDUAL METAL ION TITRATIONS

Metal	Present, *mg*	Found, *mg*	Error, %
Ca	10·67	10·64	0·3
		10·66	0·1
		10·68	0·1
Cd	29·42	29·55	0·4
		29·63	0·7
		29·55	0·4
Cu	15·91	15·76	0·9
		16·08	1·1
		16·03	0·8
		15·76	0·9
Ni	18·66	18·64	0·1
		18·64	0·1
		18·68	0·1
Pb	58·05	58·40	0·6
		58·50	0·8
Ba	27·53	28·12	2·1
		28·21	2·3
		27·92	1·4
		28·12	2·1
Mg	5·580	5·545	0·5
		5·534	0·9
		5·545	0·5
Zn	11·57	11·46	1·0
		11·54	0·3
		11·46	1·0
Bi	56·44	57·10	1·1
		56·74	0·5
		56·98	1·0

In this mixture, two metals are selectively titrated in the same buffer system at two different pH values. Since the pH range is narrow, the break at the equivalence point is very shallow. Nevertheless, it serves to prove that only small pH differences may permit selective titrations, and it emphasises the importance of pH control.

Copper and nickel: Copper and nickel may be selectively titrated in the presence of magnesium. To a solution containing approximately 0·25 mmoles of each metal ion, add 10 ml of 0·5*M* potassium acid phthalate buffer, dilute to 50 ml with 0·1*N* KNO_3, and adjust the pH to 5·5. Apply a potential of 0·25 V *vs.* S.C.E., and titrate copper with trien. Add 7 ml of 1*M* ammonia buffer and adjust the pH to 9·3. The volume of the solution should be about 70 ml at this point. Titrate nickel with trien at a potential of 0·002 V *vs.* S.C.E. (see Fig. 5). Magnesium cannot be titrated at this point with another chelon such as EDTA. Apparently EDTA replaces some of the trien combined with nickel or copper ions before reacting with magnesium. Consequently, no well-defined end-point is obtained. The sum of copper, nickel, and magnesium may be easily obtained by titrating the mixture with EDTA in ammonia at a pH of 9·3 and a potential of 0·002 V *vs.* S.C.E.

Calcium, zinc and copper: To a solution containing approximately 0·25 mmoles of each metal ion, add 10 ml of 0·5*N* potassium acid phthalate buffer, dilute to 50 ml with 0·1*N* KNO_3, and adjust the pH to 5·5. Titrate copper with trien at an applied potential of 0·25 V *vs.* S.C.E. Add 7 ml of 1*M* ammonia buffer, adjust the pH to 9·3, apply a potential of 0·002 V *vs.* S.C.E., and titrate nickel with trien. Without changing any of the existing conditions after the nickel end-point, titrate calcium with EDTA. The results of a titration of this type are shown in Fig. 6 and Table III.

Nickel and zinc: To a solution containing approximately 0·25 mmoles of each metal ion in 60 ml of 0·1*N* KNO_3, add 40 ml of 0·5*M* potassium acid phthalate buffer and adjust the pH to 5·8. Titrate nickel with tetren at an applied potential of 0·22 V *vs.* S.C.E. Add 10 ml of 0·1*M* triethanolamine, adjust the pH to 7·8, and titrate zinc at an applied potential of 0·06 V *vs.* S.C.E.

This nickel-zinc ion analysis is interesting because the effective log *K* values for Ni-tetren and Zn-tetren differ by only 2·4 units. Potentiometrically a difference of 4 units is necessary for a selective titration using only the pH effect for selectivity. As would be expected, there is a great deal of rounding near the nickel end-point. Because of this, it is necessary to exceed the nickel end-point by more than the usual amount of chelon in order to obtain a linear curve, *i.e.*, where the current is diffusion-controlled. Consequently, the zinc concentration in the mixture must be sufficient to ensure that, when the pH is changed to 7·8 after the nickel end-point, enough uncomplexed zinc still remains to define the base line for zinc (see Fig. 9). The results of such a titration are given in Table III.

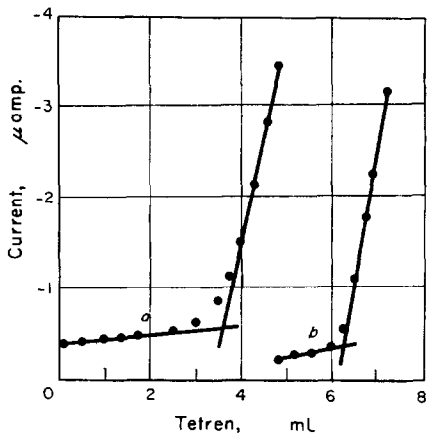


FIG. 9.—Titration of a Ni-Zn mixture.
A. Titration of Ni^{2+} in phthalate buffer at pH 5·5 with tetren.
B. Titration of Zn^{2+} in ammonia buffer at pH 9·3 with tetren.

CONCLUSION

The use of the anodic chelon wave as the indicator wave in amperometric titrations extends the usefulness of amperometric analysis by including those metal ions that exhibit ill-defined reduction waves. Futhermore, mixtures of metal ions whose log *K* values differ by *less* than 4 units can be titrated selectively, a procedure that is not practical by potentiometric analysis. This method allows the choice of both buffers and chelons in order to obtain optimum selectivity. The time required for an analysis is much less than for the usual amperometric methods since dissolved oxygen need not be removed from the system and the solution can be stirred continuously.

A primary disadvantage of the method is the interference from halide ions. However, with reasonable care, this difficulty is avoided by excluding halide ions from the analytical solution.

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Zusammenfassung—Die anodischen Wellen von Chelonen können als Indicator-wellen in amperometrischen Titrationen verwendet werden, wenn das Metallion schlecht definierte Reduktionswellen zeigt. Mittels dieser Methode ist es auch möglich Mischungen von Metallionen selktiv zu titrieren, deren log K-Werte einen kleineren Unterschied als 4 Einheiten zeigen.

Geeignete Wahl von Chelon und Puffer erlaubt Erhöhung der Selktivität. Die Methode ist rascher als die übliche amperometrische Titration.

Ergebnisse för ausgewählte Ionen und Ionenmischungen werden mitgeteilt. Es wird gezeigt wie Störungen durch Halidionen ausgeschaltet werden.

Résumé—Les vagues anodiques des "chelons" peuvent être utilisées comme indicatrices dans le titrage ampérométriques des ions métalliques qui présentent des vagues de réduction mal définies. Par cette méthode, des mélanges d'ions métalliques dont les valeurs de log K diffèrent de moins de 4 unités peuvent être titrés sélectivement. Les tampons et les "chelons" peuvent être choisis de manière à améliorer la sélectivité; cette méthode est plus rapide que les techniques ampérométriques usuelles. Des résultats sont donnés pour certains ions et mélanges d'ions. L'interférence des halogénures peut être éliminée.

REFERENCES

[1] J. Goffert, G. Michel and G. Duyckaerts, *Analyt. Chim. Acta*, 1954, **26**, 741.
[1a] G. Guerrin, M. V. Sheldon and C. N. Reilley, *Chemist-Analyst*, 1960, **49**, 36.
[2] J. H. Holloway and C. N. Reilley, *Analyt. Chem.*, 1960, **32**, 249.
[3] Hans B. Jonassen, Fred W. Frey and Anneke Schaafsma, J. *Phys. Chem.*, 1957, **61**, 504.
[4] Daniel M. H. Kern, *J. Amer. Chem. Soc.*, 1954, **67**, 4208.
[5] H. A. Laitinen and R. F. Sympson, *Analyt. Chem.*, 1954, **26**, 556.
[6] G. Michel, *Analyt. Chim. Acta*, 1954, **10**, 87.
[7] R. Přibil and B. Matyska, *Coll. Czech. Chem. Comm.*, 1951, **16**, 139.
[8] Charles N. Reilley and J. H. Holloway, *J. Amer. Chem. Soc.*, 1958, **80**, 2917.
[9] Charles N. Reilley and R. W. Schmid, *Analyt. Chem.*, 1958, **30**, 947.
[10] Charles N. Reilley, William G. Scribner and Carol Temple, *ibid.*, 1956, **28**, 450.
[11] R. W. Schmid and Charles N. Reilley, *ibid.*, 1957, **29**, 265.
[12] G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, 1954, **37**, 937.

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THERMOGRAVIMETRIC ANALYSIS OF POTASSIUM HYDROGEN PHTHALATE

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Summary—The decomposition of potassium hydrogen phthalate in nitrogen yields potassium carbonate and a char at 800° when carried out in a thermobalance at a heating rate of 300° per hr. In air, only potassium carbonate is obtained at this temperature. The rate of decomposition in carbon dioxide is ~15 mg/g/hr at 235°. These results are compared with previous work.

INTRODUCTION

THE thermogravimetric pyrolysis of potassium hydrogen phthalate in *nitrogen* has been reported[1] to proceed in three stages which are: (1) the formation of dipotassium phthalate and the volatilisation of phthalic anhydride and water; (2) the decomposition of dipotassium phthalate to yield volatile products and a residue of potassium carbonate and carbon (or "tar"); and, (3) the loss of the carbon leaving a residue of potassium carbonate in the stoichiometrically correct amount. The loss of carbon in the third step is rather surprising for a pyrolysis in nitrogen, and strongly suggests that the atmosphere was contaminated with oxygen. In an earlier paper, Erdey and Paulik[2] reported difficulty in maintaining an air-free nitrogen atmosphere in their study of the pyrolysis of BaC_2O_4 and MnC_2O_4.

There is also a disagreement about the initial decomposition temperature of potassium hydrogen phthalate. The most recent value, 190°, is claimed to be more precise than values measured by conventional thermoanalytical methods which range from 125° to 235°.

A third peculiarity of this system is the unexplained weight gain maximum at about 450° shown in the thermogravimetric curves published by Dupuis and Duval[3,4] for the intermediate decomposition product of dipotassium phthalate heated in air.

EXPERIMENTAL

The work was done with a pen-recording Chevenard thermobalance whose construction and performance have been described.[5] Experiments in static air were performed using a quartz liner tube and transparent top plate,[6] and in some cases with a quartz protective sleeve for the support rod as described by Soulen and Mockrin.[7] Experiments in controlled atmospheres were performed using a quartz tube as described by Duval,[8] modified by the addition of the quartz protective sleeve for the support rod. Even with this protective sleeve, which was very helpful, difficulty in obtaining good thermograms was sometimes experienced because the phthalic anhydride formed in the first stage of decomposition tended to deposit as long flexible needles which bridged the gap between the support rod and the wall of the sleeve and interfered with the motion of the balance. Coors porcelain crucibles were used, directly or with a platinum foil boat in the bottom. All weight changes were corrected for apparent weight gain. The potassium hydrogen phthalate was Bureau of Standards sample 84d. Samples weighing 0·1 g were used. Nitrogen was from the laboratory supply, and the carbon dioxide was the regular grade supplied by the Liquid Carbonic Co.

DISCUSSION

The thermogram of potassium hydrogen phthalate, $C_8H_5O_4K$, heated in flowing air in a platinum boat held in a porcelain crucible, is shown in Fig. 1, curve 1, and other results for Run 1 are given in Table 1. The thermogram is very similar to that previously published[1] for a sample heated in nitrogen, and with the support of the additional results given below suggests that the atmosphere they used may have contained oxygen. None of the three major intermediate plateaus is horizontal, as also shown in the earlier work,[1] so that agreement between theoretical and observed weight changes is affected by the selection of the point chosen for calculation. The curve may be interpreted as showing four major reactions in sequence: (1) the first weight loss results from the volatilisation of water and phthalic anhydride and the formation of a residue of dipotassium phthalate; (2) the second weight loss is caused by the decomposition of this compound to K_2CO_3 and char; (3) the char loses weight slowly and finally burns producing a third sharp weight loss and a residue of potassium carbonate; (4) the potassium carbonate decomposes with evolution of CO_2. In the last step the K_2O is "fixed" by reaction with the porcelain crucible which, by its roughened and crazed interior surface, clearly shows evidence of attack. The final product is indicated in the table and figure by "$[K_2O]$."

When a sample of $C_8H_5O_4K$ was heated in static air in a porcelain crucible without a protective sleeve on the crucible support rod a weight gain was obtained at *ca.* 425-450° as shown by the dashed line, Fig. 1, curve 2. However, when samples were run in static air, flowing N_2, or flowing CO_2 using a protective sleeve for the crucible support rod, this effect did not appear. It therefore seems likely that the effect is caused by evaporation of phthalic anhydride from the furnace walls with increasing temperature and its condensation on the crucible support rod. This probably also accounts for the generally smaller weight loss compared to 1 in the range 500-850°. Curve 2 otherwise follows curve 1 quite closely to about 870° when direct reaction of K_2CO_3 with the crucible occurs with volatilisation of CO_2.

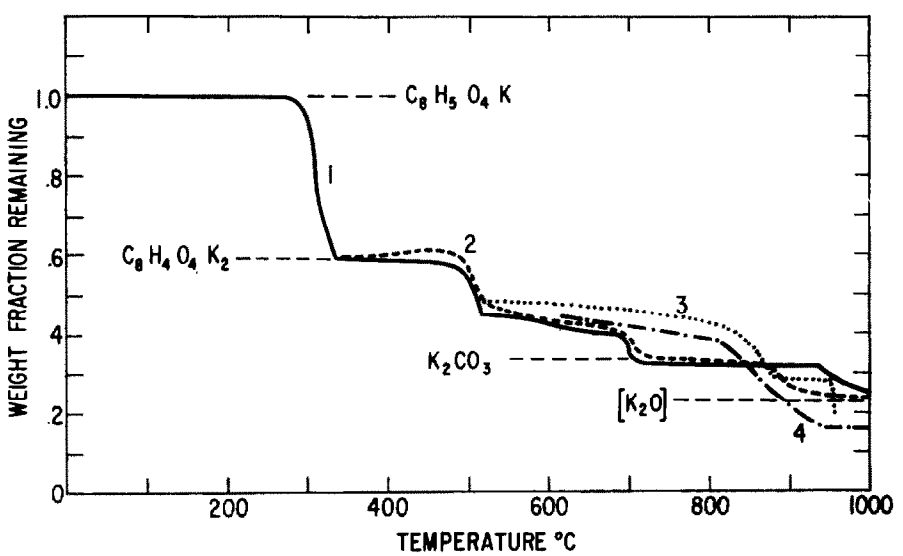


FIG. 1.—Thermograms of 0·1-g samples of potassium hydrogen phthalate at a heating rate of 300°/hr. See Table I for conditions.

TABLE I. DECOMPOSITION OF POTASSIUM HYDROGEN PHTHALATE

Substance	% Residue, calculated	Run 1 Flowing air. Platinum boat		Run 2 Static air. Porcelain crucible		Run 3 Flowing N_2 Porcelain crucible		Run 4 Flowing N_2 Platinum boat	
		T, °C	% Residue	T, °C	% Residue	T, °C	% Residue	T, °C	% Residue
$C_8H_4O_4K_2$	59·3	400	59	400	60	400	60	400	56
K_2CO_3 + Char	—	520	44	—	—	530	48	535	46
								700	42
K_2CO_3	33·8	900	32	700	36	900[b]	29	—	—
$[K_2O]$	23·1	1040 max.	23[a]	1000 max.	23[a]	—	—	—	—
C[d]	14·7	—	—	—	—	950 max.	20[a,c]	1000 max.[a]	17

[a] Based on final weighing on an analytical balance.
[b] $[K_2O]$ + char
[c] Air introduced at the end of the run to burn off char. Reaction complete in 1 min.
[d] Assuming $C_8H_4O_4K_2 \rightarrow 2K + 3CO + H_2O + H_2 + 5C$

A sample of $C_8H_5O_4K$ heated in flowing nitrogen in a porcelain crucible gave a thermogram similar to that in flowing air up to about 500°, but deviated thereafter as shown by the dotted line in Fig. 1, curve 3. In this run, the relative stability of the char in nitrogen is clearly shown and a sharp weight loss is not observed in the region of 700° as in air. The loss in weight from 500° to 880° results both from further decomposition of the char, of K_2CO_3, and also from the K_2CO_3—char reaction. The residue weight in N_2 was constant at 950°, but the char burned very rapidly when air was admitted. The final residue weight was less than that expected and the crucible was left with a shiny black interior. This would seem to be indirect evidence for the formation of potassium, by the K_2CO_3—char reaction, and its attack of the crucible.

In order to avoid completely the interference from phthalic anhydride formed in the first stage of decomposition, a sample of $C_8H_5O_4K$ in a platinum boat in a crucible was heated in an air oven for 1·5 hr at 300°. The residue was 57·9% compared to 59·3% calculated for $C_8H_4O_4K_2$. This residue in its platinum boat and crucible, when heated in flowing nitrogen, gave thermogram 4 in Fig. 1. This resembles thermogram 3 up to about 880°, but above this temperature it continues to lose weight. This undoubtedly arises from continuance of the $K_2CO_3 + C$ reaction, whereas, in thermogram 3, the K_2CO_3 had been partially consumed by reaction with the crucible. The final product at 1000° was a black porous char in the platinum boat, and a shiny black interior on the porcelain crucible containing the boat. In this run as in run 3, the quartz protective sleeve was also badly attacked.

The reaction between K_2CO_3 and graphite has been studied by Kröger and Fingas.[9] In vacuum, the strong evolution of potassium was noted as low as 700°. The CO pressure increased rapidly above this temperature, was dependent on the sample size, and the reaction was not reversible. In the thermogravimetric runs in nitrogen, the onset of this reaction is obscured, because it overlaps the gradual weight loss from pyrolysis of the char, but it is evident at least as low as 750°. In air, of course, this reaction does not occur because of the prior removal of the char by oxidation.

If the reaction observed in the earlier work[1] above 700° is in fact an oxidation, this would cause the large exothermic effect which they observe by DTA. The complex DTA curves which they report cannot thus be easily interpreted without further experiments.

Fig. 1 shows a procedural decomposition temperature[10] of ~260° for potassium hydrogen phthalate. This is the temperature at which a weight loss was first detected dynamically, and may be compared with 170°,[3] 236°,[4] and 190°[1] observed by others. These differences are not surprising, and the probable causes for this sort of difference have been discussed previously.[11] Such numbers are of little value in deciding the safe, long-term drying temperature for a primary standard substance.

The initial isothermal rate of decompositon of potassium hydrogen phthalate in carbon dioxide at 235° was measured to be ~15 mg/g/hr. Previous studies by Caley and Brundin[12] plotted as log rate *vs.* 1/T in the range 149-199° may be extrapolated to give an initial decomposition rate in air of 7 mg/g/hr at 235°. The agreement is sufficient considering the great difference in experimental conditions. Duval[4] made isothermal runs at 150°, 160°, and 170°, and observed no weight loss in 3 hr. If a sample weight of 0·5 g is assumed for his experiments, the changes expected from the results of Caley and Brundin are 0·004 mg, 0·011 mg, and 0·030 mg. These

changes are too small to be detected on the usual Chevenard thermobalance. It is therefore not surprising that Duval observed no weight changes and his observations do not conflict with those of Caley and Brundin. The only evidence contradictory to their recommendation that potassium hydrogen phthalate may be dried safely at 135° is the statement by Kolthoff[13] that the purified compound is dried at 125°, but not higher, since sublimation of phthalic anhydride takes place.

Zusammenfassung—Die Zersetzung von Kaliumhydrogenphthalat in Stickstoff gibt Kaliumcarbonat und Kohle bei 800°C, Dies wurde in einer Thermowaage mit einer Heizgeschwindigkeit von 300° per Stunde gefunden. In Luft wird nur Kaliumcarbonat erhalten. Die Zersetzungsgeschwindigkeit in Kohlendioxyd is etwa 15/mg/g/h bei 235°C. Die Ergebnisse werden mit früheren Untersuchungen verglichen.

Résumé—La décomposition du phthalate acide de potassium dans l'azote donne du carbonate de potassium et un produit de carbonisation à 800°C, quand elle est réalisée dans une thermobalance à la vitesse de chauffagede 300°C par heure. Dans l'air, seul le carbonate de potassium est obtenu à cette température. La vitesse de décomposition dans l'anhydride carbonique est environ 15 mg/gm/h à 235°C. Ces résultats sont comparés à ceux d'un travail antérieur.

REFERENCES

[1] R. Belcher, L. Erdey, F. Paulik, and G. Liptay, *Talanta*, 1960, **5**, 53.
[2] L. Erdey and F. Paulik, *Acta Chim. Acad. Sci. Hung.*, 1955 **7**, 27.
[3] M. Th. Dupuis and C. Duval, *Chim. Anal.*, 1951, **33**, 189.
[4] C. Duval, *Analyt. Chim. Acta*, 1955, **13**, 32.
[5] E. L. Simons, A. E. Newkirk, and I. Aliferis, *Analyt. Chem.*, 1957, **29**, 48.
[6] A. E. Newkirk, *ibid.*, 1958, **30**, 162.
[7] J. R. Soulen and I. Mockrin, Technical Report No. 12 to Office of Naval Research, Pennsalt Chemicals Corporation, February 4, 1960.
[8] C. Duval, *Inorganic Thermogravimetric Analysis*. Elsevier, New York, 1953. p. 26.
[9] C. Kröger and E. Fingas, *Z. anorg. Chem.*, 1933, **212**, 269.
[10] C. D. Doyle, *Analyt. Chem.*, 1961, **33**, 77.
[11] A. E. Newkirk, *ibid.*, 1960, **32**, 1558.
[12] R. Caley and H. Brundin, *ibid.*, 1953, **25**, 142.
[13] I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*. Interscience, N.Y., 1947. Vol. II, p. 94.

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SHORT COMMUNICATIONS

Tetramethylguanidine: A new solvent for titration of weak acids

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INTRODUCTION

THE titration of weak acids in non-aqueous media has been investigated by several workers.[1-4] In these previous studies the solvents used were ethylenediamine or pyridine. The necessity for the removal of small amounts of water in the titration of very weak acids and the hazardous nature of ethylenediamine are factors which limit its use. Pyridine is quite useful for the titration of all types of acidic compounds, but its offensive odour and its more hazardous nature present objections to its use. 1,1,3,3-Tetramethylguanidine (TMG) is a much less volatile material (B.P. = 159–160°) and may be used quite successfully in the presence of small amounts of water.

The titrants were standardised against benzoic acid using TMG as a solvent. In order to test the effectiveness of TMG for the titration of weak acids, various phenols were selected.

EXPERIMENTAL

Reagents and apparatus

The tetramethylguanidine was obtained from the American Cyanamid Company and purified by distillation. This material boiled between 159–161° at a barometric pressure of 738 mm. The commercial reagent was also used without any change in titrimetric properties.

The titrants used were tetrabutylammonium hydroxide, prepared according to the procedure of Harlow,[2] and the commercially available tetramethyl-ammonium hydroxide pentahydrate (South-western Analytical Chemical Company, Austin, Texas) dissolved in 4:1 benzene-methanol. Much larger end-point inflections were obtained using the tetrabutylammonium hydroxide. Most of the phenols were "white label" from Eastman Kodak, and were used without further purification.

Although preliminary potential measurements were made using the Beckman Model "G" pH meter, most of the titrations were performed using a Beckman "zeromatic" pH meter. A Beckman general purpose glass electrode No. 4990-80 was used for all the titrations. The Beckman fibre-type calomel electrode No. 39170 was used with saturated aqueous potassium chloride and a saturated solution of potassium chloride in methanol, designated hereafter as the modified calomel electrode. A 180-ml Berzelius beaker equipped with a rubber stopper was used as the titration cell. Two holes were bored in the stopper to house the electrodes; additional holes were bored for the burette, nitrogen inlet and outlet. A magnetic stirrer was used for all titrations.

Procedure

A sample containing 1 to 2 mequiv of acid was weighed into a 180-ml Berzelius beaker. Fifty ml of TMG were pipetted into the titration cell, and the system was deaerated with nitrogen. An atmosphere of nitrogen was maintained throughout the titration to prevent the absorption of carbon dioxide. The blank was determined for each series of titrations.

RESULTS AND DISCUSSION

All of the acids titrated produced satisfactory potential inflections in the region of the equivalence point, as indicated in Fig. 1. The dissociation constants of these phenols in water vary from 10^{-4} to 10^{-10}, thus indicating the wide range of acidity over which this solvent may be employed. Table I indicates the reliability of this solvent for the titration of weak acids. Titration curves with the distilled or undistilled solvent were identical.

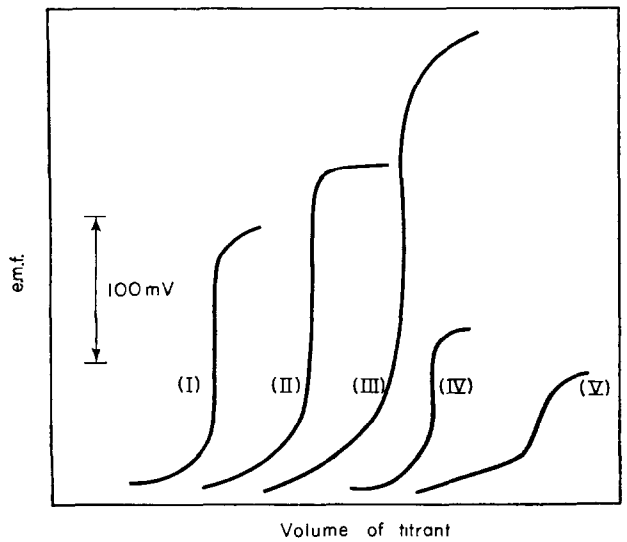


FIG. 1.—Titration of phenols with tetrabutylammonium hydroxide.
(I) β-Naphthol
(II) 2,4-Dichlorophenol
(III) *p*-Bromophenol
(IV) 2,4-Dibromophenol
(V) *p*-Nitrophenol
(VI) *m*-Nitrophenol
(VII) Phenol

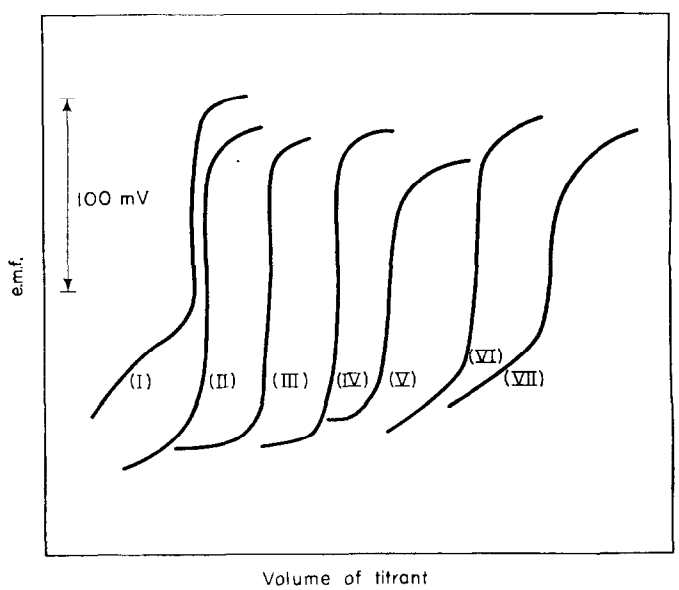


FIG. 2.—The effect of water on the end-point inflection of the titration of dinitrophenol with tetrabutylammonium hydroxide.
(I) Anhydrous TMG with glass-modified electrode
(II) Anhydrous TMG with glass-calomel electrode
(III) 1% Water in TMG with glass-modified calomel electrode
(IV) 3% Water in TMG with glass-modified calomel electrode
(V) 10% Water in TMG with glass-modified calomel electrode

TABLE I

	Compound	Taken, *g*	Found, *g*	Recovery, %
1.	2,4-Dinitrophenol	0·2154	0·2154	100·2
2.	2,4-Dinitrophenol	0·2180	0·2195	100·7
3.	Succinic acid	0·0468	0·0461	98·5
4.	*p*-Bromophenol	0·2227 0·2223	0·2175 0·2170	97·66 97·61
5.	2,4-Dichlorophenol	0·2004	0·1976	98·60
6.	2,4-Dichlorophenol	0·2090	0·2074	99·47
7.	Phenol	0·2259	0·2252	99·69
8.	Phenol	0·1822	0·1811	99·40

One may observe from Fig. 2 that small amounts of water, up to about 1%, are advantageous rather than harmful to the electrode response. Larger amounts of water have a deleterious effect on the electrode response. Further work is being performed to gain more information concerning the properties of this solvent.

Acknowledgements—The author would like to express appreciation to the American Cyanimid Company for the initial samples of TMG and to Helen Li for help with the experimental work.

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Summary—The use of 1,1,3,3-tetramethylguanidine (TMG) as a solvent for the titration of various phenols is described. The glass-calomel electrode system is employed using tetrabutylammonium hydroxide or tetramethylammonium hydroxide as the titrant. The effect of water on the electrode system is discussed. The commercially available solvent may be used without further purification.

Zusammenfassung—Die Verwendung von 1,1,3,3-tetramethylguanidin (TMG) als Lösungsmittel für die Titration verschiedener Phenole wird beschrieben. Ein Glas-Calomelelektroden-Kombination wird verwendet; Tetramethylammoniumhydroxyd ist das Titrationsmittel. Der Einfluss von Wasser auf das Elektrodensystem wird diskutiert. Käufliches Lösungsmittel kann ohne weitere Reinigung verwendet werden.

Résumé—Les auteurs décrivent l'utilisation de 1,1,3,3-tétraméthylguanidine (TMG) comme solvant pour le titrage de différents phénols. Le système d'électrode verre-calomel est utilisé; l'agent titrant est l'hydroxyde de tétrabutylammonium ou l'hydroxyde de tétraméthylammonium. L'influence de l'eau sur le système d'électrodes est discutée. Le solvent dont on dispose dans le commerce peut être utilisé sans purification.

REFERENCES

[1] D. B. Bruss and G. E. A. Wyld, *Analyt. Chem.*, 1957, **29**, 232.
[2] G. A. Harlow, C. M. Noble and G. E. A. Wyld, *ibid.*, 1956, **28**, 784.
[3] *Idem, ibid.*, 1956, **28**, 787.
[4] J. S. Fritz and S. S. Yamamura, *ibid.*, 1957, **29**, 1079.

Photophotometric titrations

(*Received* 14 *October* 1961. *Accepted* 21 *October* 1961)

A PHOTOELECTRIC titrator (such as that described by Flaschka and Sawyer[1]) employing a 1N2175 silicon photoconductive cell as detector with a low voltage battery as power supply can be markedly increased in sensitivity to light changes if the battery is replaced by a series of silicon photovoltaic cells (in the present work two "Heliodynes" consisting of eight silicon wafers each) also illuminated by light transmitted through the solution titrated (Fig. 1). Then an increase in transmitted light not only

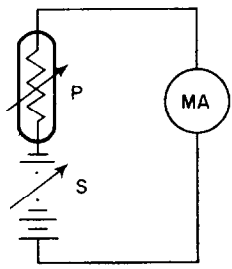


FIG. 1.—Electrical circuit for photophotometric titrations.
P, 1N2175 photoconductive cell; S, a series of two Heliodynes; MA, 0-200 microammeter.

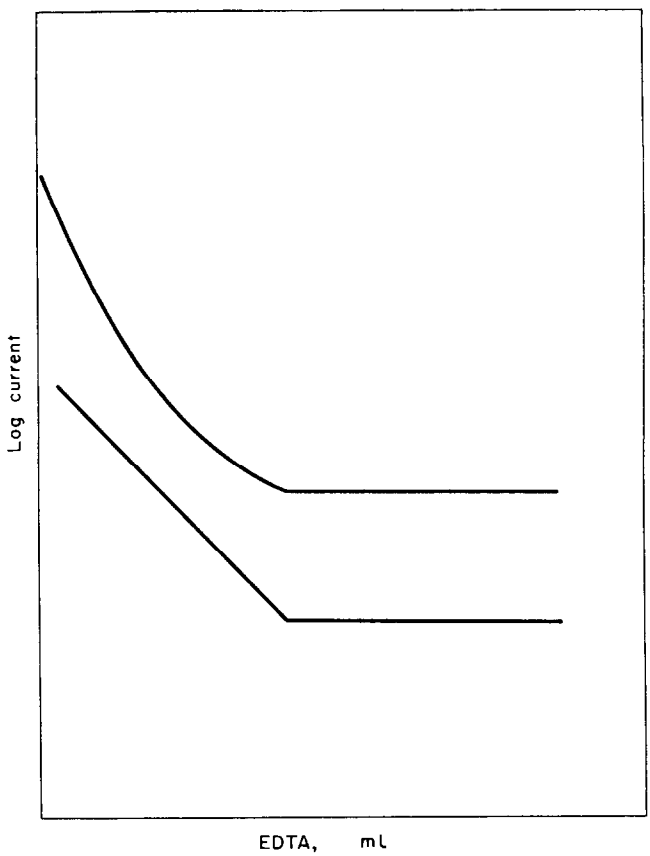


FIG. 2.—Photometric titrations of Cu with EDTA.
Upper curve, with circuit of Fig. 1; lower curve, with 4.0-V battery in series with photoconductive cell.

decreases the resistance of the photoconductive cell but also increases the supply voltage from the photovoltaic cells. Despite the considerable impedance mismatch, the combination substantially increases high transmittancy readings and decreases low ones, as compared with results using the photoconductive cell and battery. In some circumstances the combination can give an improvement in photometric end-point sharpness.

Since the peak spectral response of both types of photocells is in the vicinity of the visible-near infrared border (975 mμ for the 1N2175; about 800 mμ for the Heliodynes) the combination should be most suitable for titrations involving considerable changes in absorbancy in the 700–800 mμ region (or higher). As representative examples, respectively, of titrations with and without indicators in this region we have titrated copper with EDTA,[1] and sodium hydroxide with hydrochloric acid using Kryptocyanine as indicator. Sample results are given in Fig. 2 (Cu-EDTA) and Fig. 3 (NaOH-HCl-indicator). In both graphs the lower curve was obtained with a 4·0-V mercury battery in place of the Heliodynes. Obviously the variable supply voltage from the Heliodynes has the effect in Fig. 2 of making the end-point approach undesirably gradual, but in Fig. 3 a much larger end-point approach results. Thus, the new combination may be recommended only for titrations in which the end-point is marked by an increase in transmitted light, and in such titrations (with or without indicators) it has an amplifying action at the end-point.

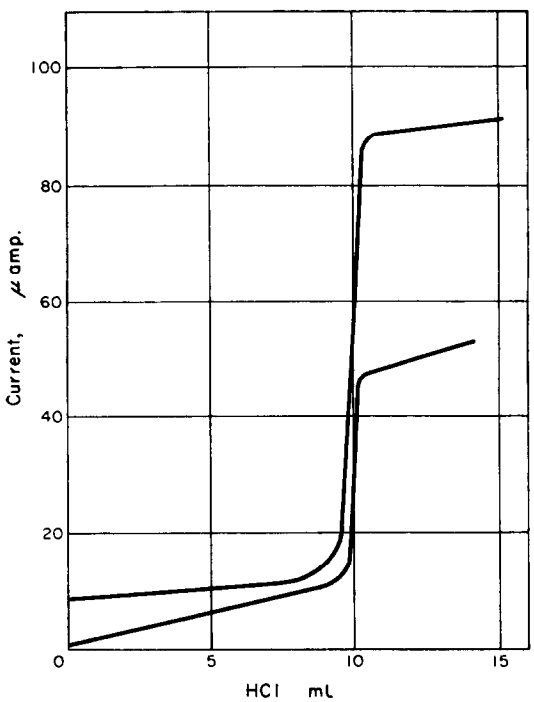


FIG. 3.—Photometric titrations of 10 ml of 0·1*N* NaOH with 0·1*N* HCl.
Upper curve, with circuit of Fig. 1; lower curve, with battery and photoconductive cell.

Another possible way to combine end-point effects from different detectors is to use a potentiometric indicator (for example, quinhydrone-calomel electrodes in an acid-base reaction) in series with the photoconductive cell (perhaps with phenolphthalein as colour indicator). The extremely low operating voltages in this case require a galvanometer to measure the current change in the titration.

EXPERIMENTAL

All titrations were performed in a 400-ml beaker illuminated by a constant-intensity white light source on one side and with the 3 photocells (total area about 1 in^2) on the opposite side, the 1N2175 being mounted in a hole drilled in a 0·5-inch thick wood block with the Heliodynes

(Lafayette Radio Corp.) attached on either side. Light intensities were large enough to allow currents up to 200 μA during a titration. Each titration was done three ways: with the Heliodynes alone (measuring voltage), with the 1N2175 cell in series with a 4·0-V battery, and with the circuit of Fig. 1. All titrations were done without benefit of filters, relying solely on the selective action of the photo cells for the 700–800 mμ region; considerable improvement might be expected if a narrow band filter appropriate to the system titrated were used.

A 200-ml portion of 0·005*M* copper sulphate was titrated with 0·1*M* EDTA,[1] taking current readings at 0·5-ml increments. The upper curve of Fig. 1 was obtained at slightly higher light intensity than the lower. In the acid-base titrations, 10 ml of 0·1*N* NaOH diluted to about 200 ml were titrated with 0·1*N* HCl, using a freshly prepared Kryptocyanine solution as indicator.

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Summary—Photometric titrations employing a photoconductive cell in series with a photovoltaic cell of approximately similar spectral response can give sharper end-points in titrations marked by an increase in transmitted light at the end-point.

Zusammenfassung—Eine instrumentelle Verbesserung für photometrische Titrationen mit Photozellen, die die Leitfähigkeit ändern, wird mitgeteilt. Die Photozelle wird mit einem Photoelement ähnlicher spektraler Empfindlichkeit in Serie geschaltet wodurch schärfere Endpunkte in photometrischen Titrationen erhalten werden.

Résumé—Les titrages photométriques utilisant une cellule photoconductrice en série avec une cellule photovoltaïque de réponse spectrale à peu près semblable peuvent donner des points équivalents plus nets, quand ceux-ci sont caractérisés par un accroissement de la lumière transmise.

REFERENCE

[1] H. Flaschka and P. Sawyer, *Talanta*, 1961, **8**, 521.

Talanta, 1962, Vol. 9, pp. 181 to 183. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEWS

Chromatography with Particular Consideration of Paper Chromatography. E. MERCK AG, Darmstadt, Germany, 1961. pp. 185, DM 18.

THIS book, which is written in English, is the second edition of a work, of which the first edition appeared as *E. Merck, Chromatographie unter besonderer Berücksichtigung der Papierchromatographie.* Although the book contains a few quaint turns of phrase and some mis-spellings such as "anorganic" for "inorganic" on p. 5, and "jodine" for "iodine" on p. 84, it is very readable. There is a brief non-theoretical description of types of chromatography, methods of column chromatography, gas chromatography, thin-layer chromatography, and electrophoresis, but the greater part of the book (118 pages) is given over to paper chromatography. The authors state that in the main, only methods proven by them are described and the large section on the separation and identification of the constituents of many classes of organic compounds using paper chromatography should be of considerable value to chemists and biochemists.

The book contains twelve excellent plates of paper chromatograms and a list of 613 references. A most useful feature of the book is a detailed list of 139 colour reagents for paper chromatography.

Since the book is published by E. Merck AG, it is not surprising that most of the chemicals and reagents which are mentioned are those supplied by that company. However, at DM 18, the book is not expensive and should be of interest to all who may wish to employ chromatographic techniques in their work.

J. B. HEADRIDGE

An Introduction to Co-ordination Chemistry. D. P. GRADDON, Pergamon Press Ltd., London, 1961. pp. 100, 25s.

THE past two decades have seen a remarkable resurgence of interest in the constitution and properties of co-ordination compounds. It is not surprising, therefore, that there should follow a number of monographs on various aspects of this rapidly growing branch of chemistry. Indeed, without the fairly frequent appearance of new texts and review articles on rather specialised topics, it would be almost impossible for research workers and teachers to keep abreast of current developments. Fortunately, several excellent books and reviews have recently become available. However, invaluable as these are to the specialist, those seeking an introduction to the subject often find them too advanced or too detailed for their purposes. It is against this background, then, that Dr. Graddon's *Introduction to Co-ordination Chemistry* makes a welcome appearance. Intended primarily for the student, it gives an exceptionally readable account of the development, the present scope and many of the more important aspects of co-ordination chemistry.

The book begins by tracing briefly the development of ideas on the constitution of complex compounds from the early eighteenth century, through Werner's classical studies, to Pauling's valence-bond theory and culminating with a simplified account of ligand-field theory. The success of the latter theory in accounting for the more outstanding features of co-ordination chemistry, *viz.* stereochemistry, magnetism, co-ordination number, *etc.*, is well illustrated. There follows a discussion of the factors determining the stabilities of complexes and an outline of the experimental methods commonly in use. The consequences of co-ordination on oxidation potentials and the stabilisation of valency states are given the emphasis they deserve. Most of the remainder of the book is devoted to an account of the constitution and bonding features of certain selected types of co-ordination compound, including carbonyls and sandwich π-complexes. The final chapter deals with some practical applications of complex formation.

Inevitably, in a short "introduction" the author is faced with the formidable problem of selection of material. He must omit much that is important and, to avoid confusion, must sometimes make non-rigorous generalisations so that it is not difficult to point to gaps and simplifications in this book. For example, it is to be regretted that the author felt compelled to omit an elementary account of the visible and ultraviolet spectra of transition metal ions; the treatment of ligand-field theory seems a

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little bare without it. However, this book must be judged not only by its treatment of individual topics, but also by how well it presents to the newcomer an idea of the extensiveness of the occurrence of co-ordination. For too long, students have tended to regard co-ordination compounds as a rather special class featuring some unique kind of dative bond. Nowadays, on any broad definition such as emerges from a ligand-field description, co-ordination can be seen to embrace almost the whole of inorganic chemistry. Dr. Graddon's book gives a useful perspective and it will, undoubtedly, be a valuable aid to students and teachers alike.

The bibliography is adequate for the non-specialist reader and the book has been attractively produced at what is nowadays an easily accessible price for the undergraduate.

S. M. NELSON

Computing Methods and the Phase Problem in X-Ray Crystal Analysis. Edited by R. PEPINSKY, J. M. ROBERTSON and J. C. SPEAKMAN, Pergamon Press Ltd., 1960. pp. viii 326, 63s.

THIS book is a collection of twenty-eight papers read at the second conference on computing methods held at Glasgow in August 1960. Most of the papers are concerned with descriptions of crystallographic programmes written for a variety of computers. The machines for which programmes are given include the IBM 650 and 704, Ferranti Pegasus and Mercury, English Electric Deuce, X-RAC, Gamma 3B–AET and the Cambridge, Cardiff and Manchester University machines. The individual programmes, which are usually described in some detail, cover the whole range of structure calculations from prediction of interplanar spacings to the application of Monte Carlo methods of structure analysis.

Those papers not directly concerned with computers include discussions of direct methods of phase determination, structure factor algebra, the heavy atom method and the phase problem in protein structures.

The book represents a comprehensive account of the state of computational methods in 1960. It should prove most useful to any crystallographer requiring up-to-date information on available computer facilities and programmes.

B. J. MCDONALD

Treatise on Analytical Chemistry, Analytical Chemistry of the Elements, Volume 3 of Part II. Edited by I. M. KOLTHOFF, and P. J. ELVING, with the assistance of E. B. SANDELL, Interscience Publishers, New York, 1961. pp. 380. $13.25. (Subscription price $12.00.)

ACCORDING to the editors, part II of the treatise critically reviews the analytical chemistry of the elements but is not intended to be encyclopædic. Section A deals with the analytical chemistry of the various elements. Volume 3 is divided into six parts, each treating an individual element. The authors of the material are W. C. Cooper (copper), G. B. Wengert, P. F. Reigler, and A. M. Carlson (magnesium), J. H. Kanzelmeyer (zinc), Q. Fernando and H. Freiser (cadium), J. F. Coetzee (mercury), and M. Farnsworth and J. Pekola (tin).

The chapters are organised according to the following uniform outline: a brief discussion of the occurrence of the element, industrial processes, toxicology, a description of the important physical and chemical properties of the element, sampling procedures, separation and isolation techniques, qualitative and quantitative analysis, discussion of selected methods for the determination of the element in alloys, ores, minerals, biological samples, *etc.*, and some detailed laboratory procedures. Unfortunately, the space devoted to the material covered (36 pages to copper, 43 to magnesium, 61 to zinc, 51 to cadmium, 82 to mercury, 38 to tin), is such that the treatment of the analytical chemistry of the elements is only cursory . Thus, there are several important analytical techniques either not referred to at all or merely mentioned in passing. Examples of neglected or inadequate treatment are the determination of copper with neocuproïne, the precipitation of cadmium and zinc with benzotriazole (this reagent is mentioned in the material on copper), Umland and Hoffman's extraction method for magnesium, and the ion-exchange separation of cadmium and zinc in an iodide medium (mentioned under zinc, but not under cadmium).

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With the exception of the excellent discussion of mercury, the book seems to offer little of value to the informed analyst.

J. O. HIBBITS

Gravimetric Methods of Chemical Analysis, in three volumes (in Hungarian). L. ERDEY. Akadémiai Kiadó, Budapest, 1960. pp. 346 + 739 + 383. 355 Hungarian Forint.

THIS book comprises all of the fundamental methods of gravimetric analysis, taking into consideration also the latest results in physical chemistry, in structural inorganic chemistry, in colloid science and in organic chemistry. The book is particularly opportune in connection with the rapid development of nuclear chemistry. This is because gravimetric analysis, regarded as micropreparative chemistry and "the science of separations," has found an extremely important field of application in nuclear chemistry.

The author discusses all of the methods critically and selects those which have particular practical importance. Results of control measurements made for critical treatment are included in tables. Most of the precipitates were investigated by means of differential thermogravimetric methods developed by the author and his co-workers.

In *Volume* I, after the introductory chapter, the author deals in detail with the successive operations of gravimetric analysis: sampling, preparation of sample, weighing, solution, fusion (the theory of high-temperature reactions is also presented), ashing and destruction of organic substances, precipitation, filtration and washing, thermal treatment of precipitates (TG, DTA and DTG methods), drying and ignition of the precipitate and weighing of the residue, calculation of errors. In the third chapter methods of separation are dealt with: fractional precipitation, organic reagents (a short but concise summary is given on the theory of complex compounds), selective dissolution, extraction (with a thorough theoretical treatment), ion-exchange resins and ion-exchange chromatography, adsorption-, partition- and paper chromatography, separation of volatile substances, indirect analysis (with an extensive mathematical treatment) and electrogravimetry (with all of its theoretical and practical problems). This Volume includes also gravimetric methods for the determination of water in solids.

In *Volume II* methods for the determination of metals are included. In some special cases micro and semimicro methods are mentioned too. Discussion of the cations follows the order of the analytical groups. The construction of each chapter is as follows: a Table (including all of the forms used for determination and the most important data for precipitation and thermal treatment), references to the methods, the forms of occurrence of the metal, preparation of the sample, detailed discussion of the procedures, thermoanalytical curves, and the accuracy of the methods. In addition, the selection of the most convenient method, the elimination of interferences, the solubility and morphology of the precipitates, the selectivity, and, finally, the methods for separation are presented. The total analysis of some raw materials and products of technological importance is discussed.

In *Volume III* are given methods for the anions. The analysis of substances containing Cl, Br, I, F, CN, SCN, S, N, P, C, Si and B, in the presence of the most frequently occurring and interfering components, is discussed, and the solution of many practical problems is presented. There is a very good summary of methods for the determination of S and Cl in organic compounds.

The appendix contains useful instructions for the handling and calculation of results.

The book is very valuable both from the theoretical and practical points of view, and, equally, both to trained experts and to beginners in analytical practice. It is an outstanding and extremely important contribution to the literature of analytical chemistry. Its translation into English and German is in progress.

E. KÖRÖS

Talanta, 1962, Vol. 9, pp. 184 to 186. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

(Material for this section should be sent directly to the Associate Editor)

ARGENTINA

Sunday–Saturday 16–22 *September* 1962: **Eighth Latin-American Congress of Chemistry,** on the occasion of the *Fiftieth Anniversary of Asociación Química Argentina.* Buenos Aires (see also **Talanta,** 1961, **8,** 909).

During the congress there will be delivered a series of general lectures by distinguished chemists, including:

Professor Dr. ING. F. FEIGEL (Brazil) — *Progress in the Spot Test Reactions of Organic Substances.*

The Section on Analytical Chemistry and Applied Analytical Chemistry has arranged special working sessions in *Catalytic Reactions induced in Analytical Chemistry* and *Optical Instrument Methods.* Latin American chemists interested in these sessions are asked to advise the Congress Organising Committee as soon as possible so that they may be placed in contact with the session organisers.

SOUTH AFRICA

Monday–Wednesday 2–11 *July* 1962: **Golden Jubilee Convention**: *South African Chemical Institute.* Johannesburg, Pretoria and Vereeniging areas.

The programme will include symposia on catalysis, reaction kinetics, crystal structure, chromatography, natural products, inorganic chemistry, analytical chemistry, biochemistry and chemical education.

Further information may be obtained from: Secretary, South African Chemical Institute, P.O. Box 3361, Johannesburg, South Africa.

UNITED KINGDOM

Wednesday 7 *March* 1962: **Annual General Meeting** followed by the **Bernard Dyer Memorial Lecture: Research and the National Economy:** Dr. D. W. HILL: *Society for Analytical Chemistry.* Midland Hotel, Manchester. 4.30 p.m.

Thursday 8 *March* 1962: **Annual General Meeting:** *Society for Analytical Chemistry, Midlands Section.* Regent House, Birmingham, 3. 6.30 p.m.

Monday 12 *March* 1962: **Recent Advances in Infrared Spectroscopy:** Dr. L. G. BELLAMY: *Royal Institute of Chemistry, Leeds Area Section.* Bradford Institute of Technology.

Friday 16 *March* 1962: **Fluorescence:** Dr. R. J. OTTER and Dr. C. A. PARKER: *Society for Analytical Chemistry, Physical Methods Group* and *Western Section,* and *Royal Institute of Chemistry, South Wales Section.* University College, Singleton Park, Swansea.

Friday 23 *March* 1962: **The History of Food Technology:** Mr. T. MCLACHLAN: *Society for Analytical Chemistry, Scottish Section.* Royal College of Science and Technology, George Street, Glasgow. 7.15 p.m.

Wednesday 28 *March* 1962: **Discussion Meeting:** *Society for Analytical Chemistry, Microchemistry Group. The Feathers,* Tudor Street, London, E.C.4. 6.30 p.m.

Thursday 29 *March* 1962: **Applications of Radio-Isotopes in Analysis:** Dr. D. GIBBONS: *Society for Analytical Chemistry, Midlands Section.* Technical College, Nottingham. 7.00 p.m.

Thursday 29 *March* 1962: **Steric Hindrance in Analytical Chemistry:** Professor H. M. N. H. IRVING: *Society of Chemical Industry, Liverpool Section,* and *Royal Institute of Chemistry, Liverpool Section* and *College Chemical and Physical Society, Carlett Park College of Further Education,* Eastham, Wirrall. 7.00 p.m.

Wednesday–Saturday 28–31 *March* 1962: **Conference on Molecular Spectroscopy:** *Institute of Petroleum, Hydrocarbon Research Group.* William Beveridge Hall, Senate House, University of London, W.C.1. (see also *Talanta,* 1962, **9,** 93).

Monday–Friday 9–13 *April* 1962: **Feigel Anniversary Symposium:** *Society for Analytical Chemistry, Midlands Section*, under the patronage of *I.U.P.A.C.* University, Edgbaston, Birmingham, 15 (see also **Talanta,** 1961, **8,** 561, 765 and 911).

The following additions and minor alterations to the scientific programme have been made:

I. P. ALIMARIN and O. M. PETRUKHIN (Moscow State University, U.S.S.R.)	*Extraction of Inner Complex Compounds of Rare Elements with N-Benzoylphenylhydroxylamine.*
J. R. AMARAL (Ministry of Agriculture, Rio de Janeiro, Brazil)	*Contribution to Organic Spot Test Analysis.*
J. BERGER (Danish School of Pharmacy, Denmark)	*Studies on S-Benzylthiouronium Salts and p-Bromophenacyl Esters for Identification of Organic Acids.*
F. CLANET (Atomic Energy Commission, Paris, France)	*Spot-Testing for Transuranic Elements.*
R. M. DAGNALL and T. S. WEST (University of Birmingham, U.K.)	*Spectrophotometric Determination of Traces of Silver.*
L. DUCRET (C.N.E.T. Laboratory, Paris, France)	*Utilisation de l'extraction pour le dosage des traces par diverses méthodes instrumentales.*
W. T. ELWELL and J. F. GIDLEY (Imperial Metal Industries Ltd.)	*Atomic Absorption Spectroscopy in Metallurgical Analysis.*
H. M. N. H. IRVING (University of Leeds, U.K.)	*Steric Hindrance in Analytical Chemistry with Special Reference to Analogues of 8-Hydroxyquinoline.*
C. A. JOHNSON (Boots Pure Drug Co., Nottingham, U.K.)	*Tetrazolium Salts in Qualitative Colorimetric Analysis.*
R. P. LASTOVFKII (Institute of Chemical Reagents, Moscow, U.S.S.R.)	*Physical-Chemical Investigation of New Complexans nad their Analytical Applications.*
A. G. LLACER (University of Rosario, Argentina)	(to be arranged).
R. L. MITCHELL (Macaulay Institute of Soil Research, Aberdeen, U.K.)	*Trace Analysis by Spectrochemical Methods.*
C. A. PARKER and L. G. HARVEY (Admiralty Materials Laboratory, Holton Heath, Poole, U.K.)	*Luminescence of Piazselenols: A New Fluorimetric Reagent for Selenium.*
D. I. RYABCHIPKOBV and L. V. BORISOVA (Moscow State University, U.S.S.R.)	*New Spectrophotometric Methods for the Determination of Rhenium based on its Complexing.*
E. SCHULEK, ZS. REMPORT-HORVATH, A. LASZTITY and E. KÖRÖS (L. Eötvös University, Budapest, Hungary)	*Increase of Limit of Identification using Collectors.*
H. SUTER (Celanese Chemical Co., Clarkwood, Texas, U.S.A.)	*Biographer of Professor Fritz Feigel.*
S. VIEBEL (Polytechnic Institute, Copenhagen, Denmark)	*Survey of Methods for the Identification of Carboxylyic Acids and Esters.*
H. WEISZ (University of Freiburg-Breisgau, Germany)	*Semi-Quantitative Analysis by Spot Reactions: A Review and New Reagents.*
C. WHALLEY (Laporte Chemicals Ltd., Luton, U.K.)	*Hydrogen Peroxide as an Analytical Reagent.*
C. L. WILSON and F. HABA (Queen's University, Belfast, N. Ireland)	*Separation and Identification of Some Anions on the Microgram Scale.*
H. N. WILSON and R. J. OTTER (I.C.I. Ltd., Billingham Division, U.K.)	*Recent Developments in X-Ray Fluorescence Analysis.*

The following lecturers have unfortunately had to withdraw from the symposium: G. V. M. DUYCHAERTS, H. FREISER and I. M. KOLTHOFF. The paper to be delivered by A. C. Menzies will be read by R. Lockyer.

The following speakers have been invited to contribute to the discussion on *Teaching of Analytical Chemistry*:

L. ERDEY, H. MALISSA, L. OTTENDORFER, H. WEISZ, P. W. WEST, C. L. WILSON, J. ZYKA

The seventeenth Annual General Meeting of the Biological Methods Group of the Society for Analytical Chemistry was held on Thursday 14 December 1961 at *The Feathers*, Tudor Street, London, E.C.4. Mr. W. A. Broom presided.

The following were elected Officers of the Group for the forthcoming year:
Chairman: Mr. J. S. Simpson
Vice-Chairman: Mr. W. A. Broom
Hon. Secretary and Treasurer: Mr. K. L. Smith, Standards Department, Boots Pure Drug Co., Ltd. Nottingham, England.

The **Annual General Meeting** of the *Western Section, Society for Analytical Chemistry*, was held at University College, Cardiff, on Friday, 12 January, 1962.
The following were elected Officers of the Section for the forthcoming year:—
Chairman: Dr. F. H. POLLARD
Vice-Chairman: Mr. E. A. HONTOIR
Hon. Secretary and Treasurer: Dr. T. G. MORRIS, Brockleigh, Clevedon Avenue, Sully, Glamorgan.

UNITED STATES OF AMERICA

Thursday 15 *February* 1962: **Trace Analysis Utilising Gas Chromatography:** Dr. D. A. MAKAY: *Metropolitan Microchemical Society.*

Friday–Saturday 2–3 *March* 1962: **Third Conference on Experimental Aspects of NMR Spectroscopy.** Mellon Institute, Pittsburgh, Pa.

Monday–Friday 5–9 *March* 1962: **Thirteenth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy:** *Analytical Chemistry Group of Pittsburgh Section, American Chemical Society* and *Spectroscopy Society of Pittsburgh.* Penn-Sheraton Hotel.

Thursday 15 *March* 1962: **An Approach to the Microdetermination of Carbon and Hydrogen:** Dr. H. F. HABER: *Metropolitan Chemical Society.*

Tuesday–Thursday 20–29 *March* 1962: **American Chemical Society, 141st National Meeting.** Washington D.C.

Wednesday–Friday 13–15 *June* 1962: **Analytical Automation and Data Processing:** *Annual Summer Symposium* of *Division of Analytical Chemistry, American Chemical Society* and *Analytical Chemistry.* College Park, Maryland.

The tentative programme is as follows:

W. J. BLAEDEL	*Automatic Enzyme Procedures.*
H. FREUND	*Continuous Automation Systems.*
K. W. GARDINER	*An Automated Instrumental Approach to Classical Chemical Analysis.*
J. HEIGL and A. L. MACRITCHIE	*Data Handling Systems for Gas Chromatography.*
D. R. JOHNSON, J. W. CASSELS, E. G. BRAME and D. F. WESTNEAT	*Automated Infrared Analysis of Polymer Films.*
H. J. NOEBELS	*Automated and Automatic Laboratory Analytical Equipment.*
H. PURDUE	*Automatic Potentiometric Reaction Rate Method—Microdetermination of Cystine.*
A. SAVITZKY	*Some Numerical Operations on Analytical Data.*
B. F. SCRIBNER	*Experience with Direct Reading Spectrometers.*
R. STELZNER	*Some Direct Readout and Linearisation Circuits in Analytical Laboratory Instrumentation.*
D. THOMAS	*Infrared Spectral Data Retrieval by Digital Techniques.*
R. E. WAINERDI	*Automatic Activation Analysis.*

Further information may be obtained from Dr. LEWIS H. ROGERS, Vitro Laboratories, West Orange Laboratory, 200 Pleasant Valley Way, West Orange, N.J.

Upon his retirement from Brooklyn College, Dr. N. CHERONIS was awarded an Honorary Membership and Scroll for outstanding contributions to the *Metropolitan Microchemical Society.* The award was presented at the Society's regular monthly meeting on January 18. 1962.

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PAPERS RECEIVED

An automatic analyser for hypophosphite with particular reference to electrodeless plating solutions S. GREENFIELD and R. M. COOPER. (2 *December* 1961).

Colorimetric estimation of cobalt as the thiocyanate complex—Part I: Use of 2-picoline as the complexing agent in aqueous solutions: M. R. VERMA and P. K. GUPTA. (5 *December* 1961).

Colorimetric estimation of cobalt as the thiocyanate complex—Part II: Use of tri-n-butyl phosphate as extractant for the complex: M. R. VERMA and P. K. GUPTA. (5 *December* 1961).

Indirect derivatographic determination of calcium, strontium and barium ions in the presence of one another: L. ERDEY, G. LIPTAY, G. SVEHLA and E. PAULIK. (6 *December* 1961).

An investigation by electron-spin resonance of the redox indicator Variamine Blue: L. ERDEY and R. C. PINK. (7 *December* 1961).

Untersuchung der Kationensorption aus Komplexanmedium III: Chromatographische Trennung von Strontium und Barium: ZDENĚK ŠULCEK, PAVEL POVONDRA und RICHARD ŠTANGL. (15 *December* 1961).

The separation and determination of chromium, tungsten, molybdenum and vanadium by partition chromatography: A. S. WITWIT, R. J. MAGEE and C. L. WILSON. (19 *December* 1961).

Determination of ^{90}strontium in bone: HARRY FOREMAN and M. B. ROBERTS. (20 *December* 1961).

ERRATA—Volume 9

Page 1, *last line of summary: the formula should read* $(NH_4)_3[Sc(C_8H_6O_3)_3]$.
Page 9, *footnote:* the reference should read *Zhur. analit. Khim.*, 1959, **14**(5), 574.
Page 26, *line* 2: *for* Sajó method[4] *read* Sajó method[5].
Page 76, *footnote:* the reference should read *Talanta*, 1961, **8**, 720.

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COULOMETRIC TITRATION OF HYDROXYLAMINE AND HYDROGEN PEROXIDE BY ELECTROGENERATED CERIC ION

TAKEO TAKAHASHI and HIROSHI SAKURAI
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(*Received* 20 *March* 1961. *Accepted* 30 *September* 1961)

Summary—Since hydroxylamine reduces Fe^{III} quantitatively to Fe^{II}, the coulometric determination of hydroxylamine may be carried out by coulometric titration of Fe^{II} with electrogenerated Ce^{IV}. Using 0·01*N* cerous sulphate-ferric sulphate and 1*N* sulphuric acid, and a constant current of 10 mA, the error of the method is found to be within about 1%. Hydrogen peroxide reacts instantaneously and quantitatively with Ce^{IV}, and can be determined with an accuracy of about 1 to 2%, provided that 0·01*N* cerous sulphate-1*N* sulphuric acid is used as an electrolytic solution and the electrolytic oxidation is carried out at a constant current of about 10 mA.

INTRODUCTION

THE first coulometric method was elaborated by Furman, Cooke and Reilley,[1] who titrated ferrous ion with electrogenerated ceric ion. This coulometric cerimetry has been applied to the determinations of $[Fe(CN)_6]^{4-}$,[2] Ti^{III},[3] As^{III},[4] I^-,[5] metol[6] and hydroquinone.[6] The authors[7] have already reported the direct coulometric cerimetry of hydroquinone and *p*-aminophenol, as well as the indirect determination of oxalic acid, β-naphthylamine and aniline.

In the present study coulometric cerimetry has been successfully applied to the determination of hydroxylamine and hydrogen peroxide. According to Szebellédy and Somogyi,[8] hydroxylamine has not previously been determined coulometrically with reagents other than bromine. The present investigation is based on the reaction between hydroxylamine and ferric ion:

$$2NH_2OH + 2Fe_2(SO_4)_3 = 4FeSO_4 + 2H_2SO_4 + H_2O + N_2O \quad (1)$$

The ferrous ion is then coulometrically titrated with electrogenerated ceric ion.

In acidic medium, hydrogen peroxide may react in two ways, *i.e.*, as an oxidising or a reducing agent, thus:

$$H_2O_2 = O_2 + 2H^+ + 2e \quad (2)$$

$$H_2O_2 + 2H^+ + 2e = 2H_2O \quad (3)$$

Ceric ion reacts with hydrogen peroxide in a similar way to potassium permanganate, according to the equation:

$$2Ce^{4+} + H_2O_2 = 2Ce^{3+} + O_2 + 2H^+ \quad (4)$$

This reaction proceeds instantaneously and quantitatively, with the evolution of oxygen. In the present investigation the reaction (4) was successfully applied using electrogenerated ceric ion.

EXPERIMENTAL

Apparatus

The titration cell, the constant current source, the stirrer and the time measuring apparatus have already been described.[7] The generating anode was a platinum electrode, 20 mm × 20 mm, and an electronic automatic balancing voltage recorder was used for measuring the potential for detection of the end-point.

Reagents

The reagents were of specially purified grade.

Water: Purified by ion-exchange.

Electrolytic solution for the determination of hydroxylamine: Dissolve ceric sulphate in 1*N* sulphuric acid until the solution is almost saturated, and to this add ferrous ammonium sulphate-sulphuric acid, 1*N*, to reduce ceric ion to cerous ion (a greater excess of ferrous ion than one equivalent must not be added). Dilute the solution with sulphuric acid (1*N*) so as to produce 0·01*N* concentrations of cerium and iron ions.

Electrolytic solution for the determination of hydrogen peroxide: Dissolve ceric sulphate in sulphuric acid (1*N*) and to this add gradually 0·01 equivalent of hydrogen peroxide to reduce ceric ion to cerous

TABLE I. THE COULOMETRIC TITRATION OF HYDROXYLAMINE

Hydroxylamine sampled, × 10^{-2} *meq*	Electrolytic time, *sec*	Amount found, × 10^{-2} *meq*	Error, %
3·810	365·8	3·738	−1·9
3·810	376·6*	3·848	+1·0
3·810	381·2*	3·895	+2·2
3·810	379·5*	3·874	+1·8
		av. 3·840	+0·8
		st. dev. 0·061	
7·619	742·8	7·590	−0·4
7·619	741·8	7·580	−0·5
7·619	749·3*	7·656	+0·5
7·619	757·1*	7·736	+1·5
		av. 7·641	+0·3
		st. dev. 0·062	
11·429	1117·3	11·416	−0·1
11·429	1112·4	11·366	−0·6
11·429	1114·9*	11·392	−0·3
11·429	1129·9*	11·545	+1·0
		av. 11·430	0·0
		st. dev. 0·072	
19·048	1869·0	19·097	+0·3
19·048	1869·8	19·105	+0·3
19·048	1874·3	19·151	+0·5
19·048	1873·8	19·146	+0·5
		av. 19·125	+0·4
		st. dev. 0·024	

ion (a greater excess of hydrogen peroxide than one equivalent must not be added). Boil the decolorised solution in order to destroy the remaining hydrogen peroxide and then dilute the cooled solution with sulphuric acid, 1*N*, to a volume of 1 litre. The solution is equivalent to 0·01*N* cerous sulphate—1*N* sulphuric acid.

Cathodic solution: Dissolve 15 g of ammonium sulphate in 85 g of water.

Hydroxylamine solution, 0·01*M*: Use hydroxylamine hydrochloride and purified water.

Hydrogen peroxide solution, 0·01*M*: Dilute concentrated hydrogen peroxide (30%) with purified water and standardise with standard potassium permanganate solution.

Experimental procedure

The detection of the end-point was carried out potentiometrically, using a platinum plate 5 mm × 5 mm as indicating electrode and a calomel electrode as reference electrode.

Determination of hydroxylamine: Take 100 ml of electrolytic solution and make its potential 0·7 V *vs.* S.C.E. If the potential is lower than 0·7 V *vs.* S.E.C., the generating electrode is used as anode and electrolytic oxidation is carried out until the potential reaches 0·7 V. If the potential is higher than 0·7 V *vs.* S.C.E., electrolytic reduction is carried out. Transfer this prepared solution into an Erlenmeyer flask (200-ml) to which the sample solution (hydroxylamine solution) is added, boil gently for 5–6 min, and return the cooled solution to the titration cell. Ferrous ion produced in the above solution is oxidised by ceric ion which is coulometrically generated at a constant current, until the potential indicates 0·7 ± 0·01 V *vs.* S.C.E. The amount of hydroxylamine can be calculated as a product of the constant current (A) and electrolytic time (sec).

Regeneration of the used electrolytic solution is carried out by adding sodium hydroxide to the used solution to make it alkaline, in order to precipitate cerium and iron as the hydroxides. These hydroxides are dissolved in sulphuric acid after filtering and washing. During this operation a small amount of cerous ion may be oxidised by oxygen in the air, so that it must be reduced electrolytically or by adding ferrous ion before its re-use. The experiments employing used electrolytic solution are shown marked with an asterisk in Table I.

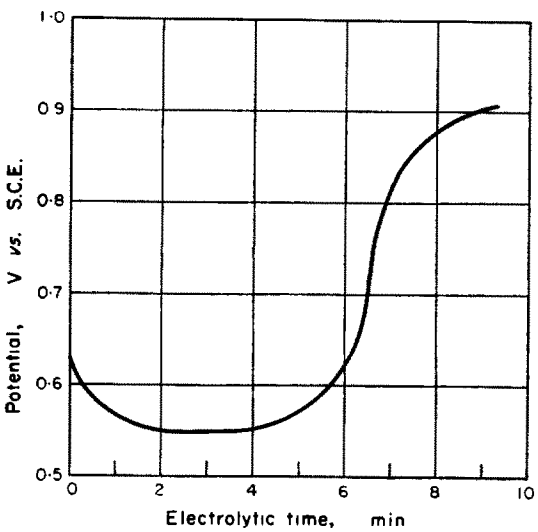


Fig.1.—Coulometric titration curve of hydrogen peroxide

Determination of hydrogen peroxide: Take 100 ml of electrolytic solution in the titration cell, oxidise electrolytically for 1–2 sec, confirming the absence of reducing substances in the electrolytic solution by observing the indicating potential. Add the sample solution (hydrogen peroxide solution), carry out electrolytic oxidation until the potential shows 0·70 V *vs.* S.C.E., and measure the amount of hydrogen peroxide as the product of the constant current and the electrolytic time. The electrolytic solution may in this case be used without regeneration for a series of successive titrations.

RESULTS

Table I shows the results for the coulometric titration of 2–10 ml of 0·01 *M* hydroxylamine solution at a constant current of 9·86 mA during the electrolytic oxidation. The results show that coulometric cerimetry can be applied to the determination of hydroxylamine with an accuracy of 1%. The same electrolytic solution cannot, however, be repeatedly employed because comparatively large errors are obtained (see Table I).

The coulometric titration curve of hydrogen peroxide with ceric ion is shown in Fig I. The potential decreases by ~50 mV from the initial potential during the titration (for 90 ~ 120 sec of the electrolytic time). This phenomenon may result from the indicated potential lag. However, the potential change shows about 300 mV at the end-point, indicating a typical type of titration curve. The reproducibility of the indicated potential before each titration shows a fluctuation of ±50 mV. This may possibly be caused by variations in absorbed oxygen on the indicating platinum

TABLE II. THE COULOMETRIC TITRATION OF HYDROGEN PEROXIDE

Hydrogen peroxide sampled, $\times 10^{-2}$ *meq*	Electrolytic time, *sec*	Amount found, $\times 10^{-2}$ *meq*	Error, %
4	380	3·883	−2·9
4	389	3·975	−0·6
4	385	3·934	−1·7
4	385	3·934	−1·7
4	387	3·954	−1·3
		av. 3·934	−1·7
		st. dev. 0·034	
8	777	7·939	−0·8
8	776	7·929	−0·9
8	776	7·929	−0·9
8	777	7·939	−0·8
8	778	7·950	−0·6
		av. 7·939	−0·8
		st. dev. 0·009	
12	1166	11·914	−0·7
12	1170	11·955	−0·4
12	1173	11·986	−0·1
12	1171	11·965	−0·3
		av. 11·955	−0·4
		st. dev. 0·026	
20	1915	19·567	−0·2
20	1920	19·618	−0·2
20	1923	19·649	−0·2
		av. 19·608	−0·2
		st. dev. 0·026	

electrode. But the end-point shows an approximately constant value, namely about 0·7 V *vs.* S.C.E.

Table II shows the results of the coulometric titration of $2 \sim 10$ ml of 0·01*M* hydrogen peroxide solution at a constant electrolytic current of 9·86 mA.

According to Table II, amounts of hydrogen peroxide larger than 10^{-4} equiv. can be determined with an error of $\pm 0{\cdot}5\%$ and the error increases to about 2% in the determination of about 5×10^{-5} equiv. of hydrogen peroxide.

The repeated use of the same electrolytic solution not only saves reagents, but decreases the interval between successive titrations. Table III gives the results of experiments in which there has been repeated use of the electrolytic solution. In

TABLE III. REPEATED USE OF THE SAME ELECTROLYTIC SOLUTION

No. of times repeated	Exp. 1, *sec*	Exp. 2, *sec*
1	380	388
2	383	388
3	383	388
4	390	386
5	382	386
6	382	388
7	388	386
8	387	390
9	389	391
10	390	391
av.	385·4	388·2
st. dev.	3·6	1·7

these experiments 2 ml of 0·01*M* hydrogen peroxide are used each time and the electrolytic oxidation (electrogeneration of ceric ion) is carried out at a constant current of 9·85 mA. As soon as one titration is complete, the next sample solution is introduced, and the next titration takes place immediately.

Zusammenfassung—Hydroxylamin reduziert einen äquivalenten Betrag von Ferri-ionen. Es ist daher möglich Hydroxylamin durch eine coulometrische Titration des gebildeten Ferroeisens mit elektrolytisch gebildetem Ceriionen zu bestimmen. Bei Verwendung einer 0·01 N Cerosulfat-Ferrisulfat Lösung, 1 N Schwefelsäure und eines konstanten Strome von 10 mA beträgt der Fehler 1%.

Résumé—L'hydroxylamine réduit une quantité équivalente de Fe (III) en Fe(II); son dosage a donc été réalisé par titrage coulométrique de Fe(II) par Ce(IV) préparé par électrolyse. En utilisant une solution contenant du sulfate céreux et du sulfate ferrique 0,01 N et de l'acide sulfurique N, et un courant constant de 10 mA, l'erreur est d'environ 1%.

L'eau oxygénée réagit instantanément et quantitativement avec Ce(IV), de sorte qu'elle peut être dosée à 1 ou 2 pour cent près à condition d'utiliser comme électrolyte une solution contenant du sulfate céreux 0,01 N et de l'acide sulfurique N, et de réaliser l'oxydation électrolytique avec un courant constant d'environ 10 mA.

REFERENCES

[1] N. H. Furman, W. D. Cooke and C. N. Reilley, *Analyt. Chem.*, 1951, **23**, 945.
[2] R. V. Dilts and N. H. Furman, *ibid.*, 1955, **27**, 1275.
[3] *Idem, ibid.*, 1955, **27**, 1596.

[4] N. H. Furman and A. J. Fenton, Jr., *ibid.*, 1956, **28,** 515.
[5] J. J. Lingane, C. H. Langford and F. C. Anson, *Analyt. Chim. Acta,* 1957, **16,** 165.
[6] N. H. Furman and R. N. Adam, *Analyt. Chem.*, 1953, **25,** 1564.
[7] T. Takahashi, K. Kimoto and H. Sakurai, *Rep. Inst. Ind. Sci., Univ. of Tokyo,* 1955, **5,** No. 6.
[8] L. Szebellédy and Z. Somogyi, *Z. analyt. Chem.*, 1938, **112,** 395.

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CONTINUOUS COULOMETRIC TITRATION OF MICRO-QUANTITIES OF IRON IN WATER

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Institute of Industrial Science, University of Tokyo
Yoyoi cho, Chiba City, Japan

(*Received* 29 *March* 1961. *Accepted* 14 *September* 1961)

Summary—Continuous determination of micro-quantities of iron dissolved in water has been investigated by means of coulometric titration with electro-generated bromine. The test solution was allowed to flow continuously through a Jones' reductor, where all of the iron in the solution was reduced to iron^{II} and was subsequently determined coulometrically with bromine. The electrolytic solution contained potassium bromide in a buffer solution of acetic acid-sodium acetate, and the end-point was detected potentiometrically with platinum-calomel electrodes. Employing the coulometric method under suitable conditions, the relationship between the amount of iron present and electrolytic current was proportional to within about 15%.

INTRODUCTION

RECENTLY it became an urgent problem to determine continuously the minute quantity of metals in feed water for high pressure boilers in power generating stations. Iron is the most common metal dissolved in the water; moreover, its continuous determination is now considered to be important in many industrial fields. The authors[1] have already reported the coulometric titration for the determination of iron^{II} by electrogenerated bromine. In practice the dissolved iron occurs in both the bi- and tervalent states. In the present study, the first part deals with the continuous coulometric titration of iron^{II} by electrogenerated bromine, and the latter part with the continuous coulometric titration of total iron, after iron^{III} has been reduced to iron^{II} by zinc amalgam.

EXPERIMENTAL

The apparatus for continuous coulometric titration has already been reported.[1] The continuous coulometric titrator (see Fig. 1) used in the present experiments incorporates an automatic titrator. The electrolyte solution (potassium bromide solution) is introduced into the electrolytic cell at a

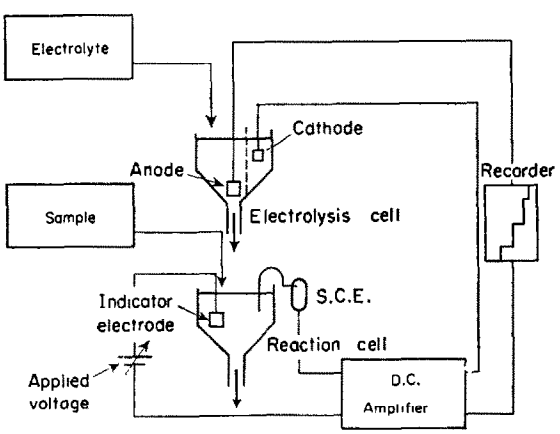


FIG. 1.—Schematic diagram of automatic continuous coulometric titrator.

definite rate, in whicn bromine is electrolytically generated on the generating anode surface, then reaches the titration cell where it is mixed with the stream of the sample solution. The titration cell is provided with a platinum indicating electrode for end-point detection and a saturated calomel electrode between which is applied a d.c. constant voltage a little above the potential of the end-point. The solution in the titration cell is always automatically controlled to contain a small excess of free bromine. The electrolytically generated bromine reacts with the reacting substance in the sample solution and the remaining bromine changes the potential between the indicating electrodes; the potential difference between the indicator and the reference potentials is fed into a d.c. amplifier (with a.c. convertor) and its output is supplied as electrolytic current for the electrogeneration of bromine.

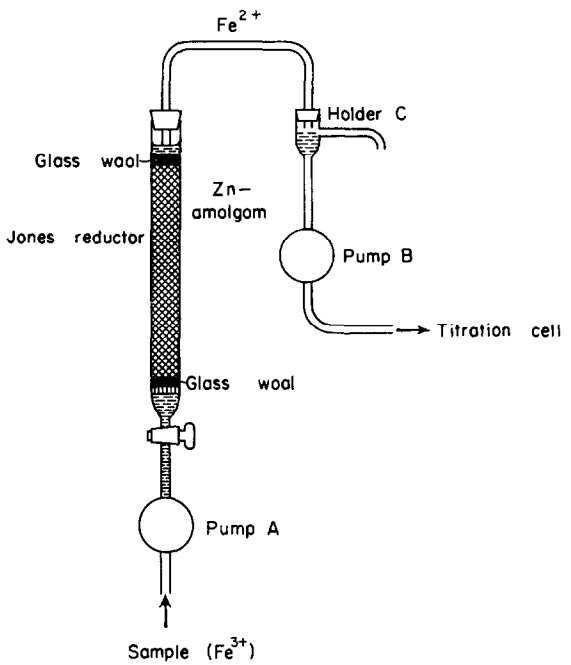


FIG. 2.—Reductor for reduction of iron^{III} ion.

The sample solution is prepared by diluting 0·01*N* ferrous or ferric ammonium sulphate-0·1*N* sulphuric acid solution with purified water. The electrolytic solution is composed of 0·1*M* potassium bromide, 1*M* acetic acid, 0·2*N* sodium hydroxide and gives a pH of about 4·2. All the reagents are of commercially pure grade and the purified water is prepared with ion-exchange resins. The solid zinc amalgam used for the reduction of iron^{III} ion is prepared by suspending 100 g of zinc granules (10 ~ 30 mesh) in 200 ml of mercuric chloride solution (2%) containing 2 ml of HNO_3 (conc.) and washing the amalgamated zinc granules very well with the purified water. The reduction is carried out by using the Jones' reductor shown in Fig. 2, the glass tube being filled with the amalgamated zinc granules. At the bottom of the glass tube (15 mm i.d. and 300 mm long) is placed a polyethylene sieve support. The amalgamated zinc granules (220 ~ 230 mm high) are supported on glass wool placed above the polyethylene sieve support. The prepared reductor is, of course, always filled with water or, alternatively, with the solution used previously, when not in use. The sample solution is fed to the bottom of the reductor at constant flow rate, using the pump A (a small pump of diaphram type made by Denkishiki Kagakukeiki Co., Tokyo) and the reduced sample solution leaves the top of the reductor, enters the small holder C, and thence passes to the titration cell at a rate of 0·16 ml/sec. The pump B is a small geared one, driven with a synchronous motor.

Dynamic working titration curve

The continuous titration curve is not necessarily the same as the single titration curve because the rate of the reaction and attainment of equilibrium has to be taken into account. A previous paper[1] disclosed the fairly large lag near the end-point in the reaction between iron^{II} ion and bromine, which varied particularly markedly with the composition of the solution. The dynamic titration curves of

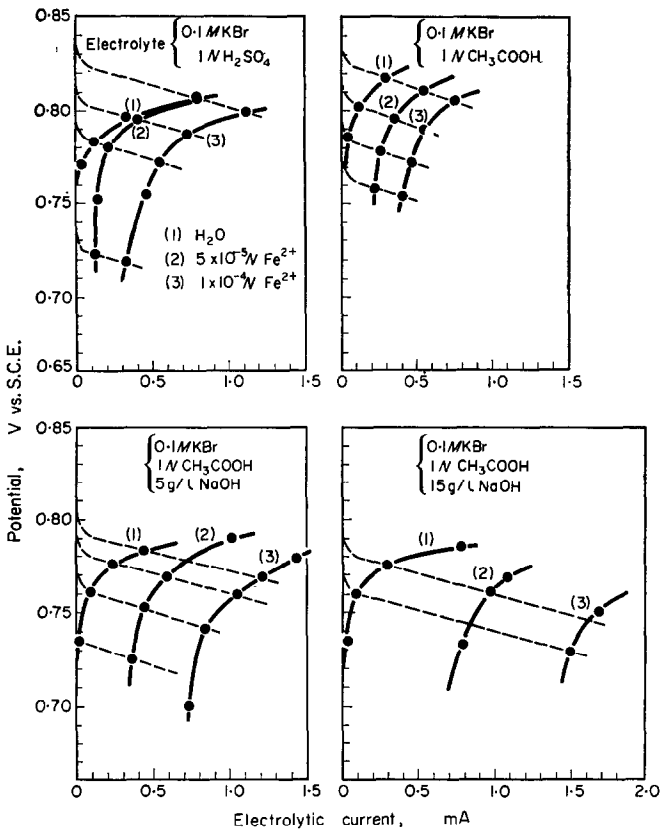


FIG. 3.—Dynamic titration curves.

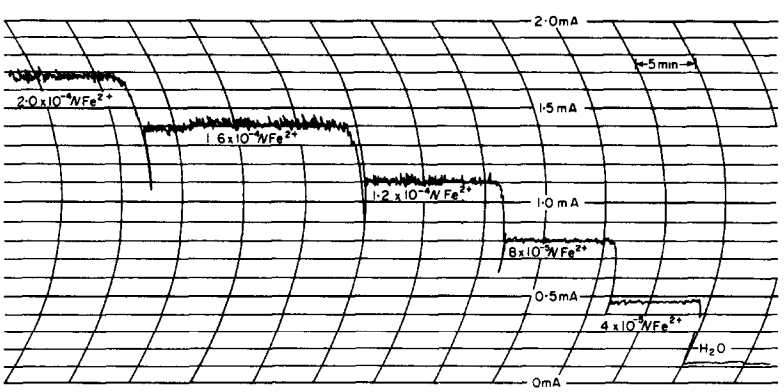


FIG. 4.—Recorded chart of the electrolysis current under various concentrations of the iron^{II} ion.

$5 \times 10^{-5}N$ and $1 \times 10^{-4}N$ iron^{II} ion in four electrolytic solutions are shown in Fig. 3. The method of preparation of these curves has been given in a previous paper.[3] The theoretical values of the electrolytic current are, respectively, about 1·5 mA and 0·75 mA in the cases of $5 \times 10^{-5}N$ and $1 \times 10^{-4}N$ iron solution.

Fig. 3 shows that the relationship between the concentration of iron^{I} and electrolytic current is more linear in acetic acid solution than in sulphuric acid solution, and approaches more nearly to the theoretical one in higher concentrations of sodium hydroxide.

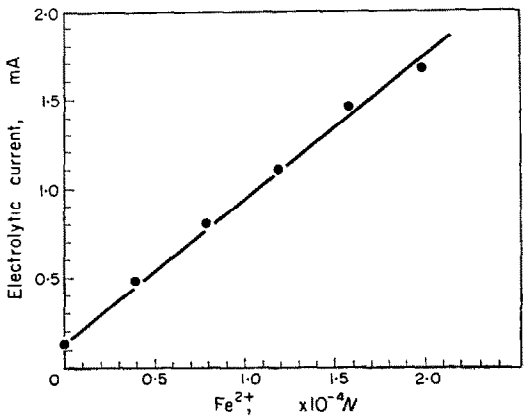


FIG. 5.—Relationship between concentration of iron^{II} ion in water and electrolysis curve.

Continuous coulometric titration of iron^{II}

Fig. 4 is the graph obtained for experiments in which iron^{II} ions were titrated in solutions composed of 0·1*M* potassium bromide, 0·1*N* sodium hydroxide and 1*M* acetic acid. The relationship between the iron concentration and electrolytic current calculated from the graph is given in Fig. 5. The results depicted in Figs. 4 and 5 show that the procedure is satisfactory for routine analysis.

Operating conditions for Jones' reductor

It was necessary to find the optimum concentration of sulphuric acid for the reduction of iron^{III} in the Jones' reductor, without interfering with the acetic acid-acetate supporting electrolyte used in the coulometric titration. At high concentrations of sulphuric acid, zinc amalgam reacts with sulphuric acid as follows:

$$H_2SO_4 + Zn \rightarrow ZnSO_4 + H_2.$$

and the evolved hydrogen gas is absorbed on the indicating platinum electrode, causing an erroneous indication of the potential. On the other hand, at small concentrations of sulphuric acid, iron precipitates as hydroxide so that the results are incorrect. In view of the importance of the sulphuric acid concentration, it was necessary to examine its effect on the reduction of the iron^{III} ion. The

TABLE I. EFFECT OF THE CONCENTRATION OF SULPHURIC ACID IN THE REDUCTION IN THE JONES' REDUCTOR.

H_2SO_4, *N*	0·01*N* $KMnO_4$ solution, *ml*			
	I-fraction	II-fraction	III-fraction	av.
0·1	9·90	9·95	9·90	9·92
0·03	9·90	9·90	9·95	9·92
0·01	9·90	9·95	9·95	9·93
0·003	9·90	9·95	10·03	9·96
0·001	9·60	9·60	9·60	9·60
0·001*	3·45	3·50	3·45	3·47
H_2O	7·50	7·50	7·45	7·48
H_2O*	3·35	3·30	3·30	3·32

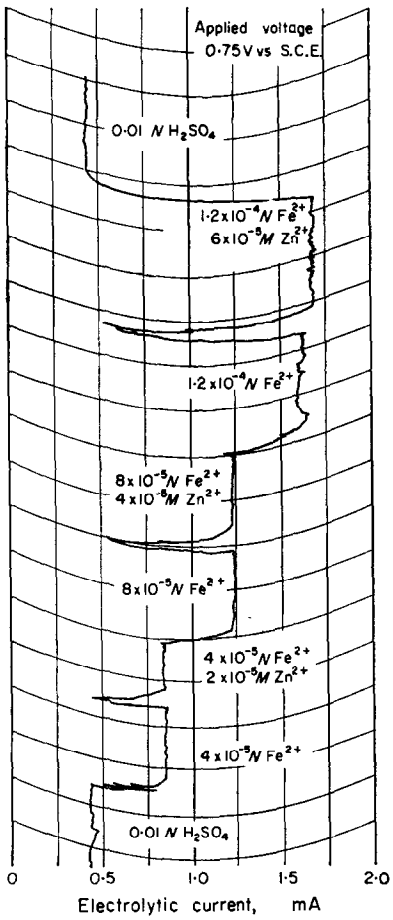


FIG. 6.—Record of continuous coulometric titrations of iron^{II} ion and iron^{II} ion plus zinc ion.

sample solution containing 0·001*M* iron^{III} ammonium sulphate and sulphuric acid of various concentrations was fed at a rate of about 20 ml per min to the bottom of the reductor. Fifty-ml fractions of the reduced solution were titrated with 0·01*N* potassium permanganate solution after adding 2 g of sulphuric acid. The results are given in Table I.

The reduction appears to be ideal when carried out in 0·1 ~ 0·003*N* sulphuric acid, but is poor in sulphuric acid when it is less than 0·001*N*. In these experiments freshly prepared solutions were used and it was noticed that the solution containing less than 0·001*N* sulphuric acid gradually formed a reddish-brown precipitate and accumulated in the reductor tube, resulting in a lowering of the concentration of iron^{II} ion in the reduced solution. In 0·1*N* sulphuric acid the evolution of hydrogen gas was observed. Sulphuric acid which was 0·01*N* seemed to be the most favourable concentration in the sample solution, because it did not markedly vary the pH of the acetic-acetate solution and the reduction of iron^{III} to iron^{II} was satisfactory.

Effect of zinc ion

Iron^{III} ion in the sample solution is reduced in the Jones' reductor according to the following reaction:

$$2Fe^{3+} + Zn \rightarrow 2Fe^{2+} + Zn^{2+}.$$

Since it was important to know whether the presence of zinc ions interfered with the reaction of iron^{II} ions with bromine, the following experiment was carried out.

Sample solutions composed of 0·1*M* potassium bromide, 1*M* acetic acid and 0·2*N* sodium hydroxide, contained iron^{II} ammonium sulphate and zinc sulphate at various concentrations. Those solutions were passed through the Jones' reductor and the electrolytic currents for electro-generation of bromine were recorded in the chart seen in Fig. 6. The results show that zinc ions in the sample solution have no effect on the coulometric titration with bromine.

TABLE II.—CONTINUOUS COULOMETRIC DETERMINATIONS OF IRON IN WATER

Sample solution used		Electrolytic current, *mA*											Av.	mA/5 × 10^{-5} eq. Fe
	$5 \times 10^{-5}M$	0·50	0·42	0·43	0·49	0·34	0·35	0·34	0·38				$0·40_6$	0·203
	1×10^{-4}	0·98	0·94	0·96	0·88	0·78	0·91	1·08	0·87	0·91	0·92*	1·02*	$0·93_2$	0·233
$Fe_2(SO_4)_3$	$1·5 \times 10^{-4}$	1·46	1·41	1·41	1·38								$1·41_3$	0·236
	$2·0 \times 10^{-4}$	1·87	1·84	1·90	1·80*	1·82*							$1·84_6$	0·231
	$3·0 \times 10^{-4}$	2·60*												0·217
	5×10^{-5}	0·18	0·18	0·19	0·21								$0·19_0$	0·190
	1×10^{-4}	0·44	0·57	0·44	0·50	0·50*	0·40*	0·41*					$0·46_8$	0·233
$FeSO_4$	2×10^{-4}	0·96*	0·78*	0·80*									$0·84_7$	0·212
	3×10^{-4}	1·15*	1·19*										1·17	0·195
	4×10^{-4}	1·50*												0·188
$Fe_2(SO_4)_3$	$FeSO_4$													
$5 \times 10^{-5}M$	$5 \times 10^{-5}M$	0·53	0·55											
1×10^{-4}	1×10^{-4}	1·13	1·29	1·46	1·30	1·52*	1·52*							0·180
1×10^{-4}	2×10^{-4}	2·01*	2·27*										1·37	0·253
2×10^{-4}	1×10^{-4}	2·50*	2·72*										2·14	0·267
2×10^{-4}	2×10^{-4}	2·92*											2·61	0·261

The applied voltage is 0·73 V but 0·75 V in the cases marked *

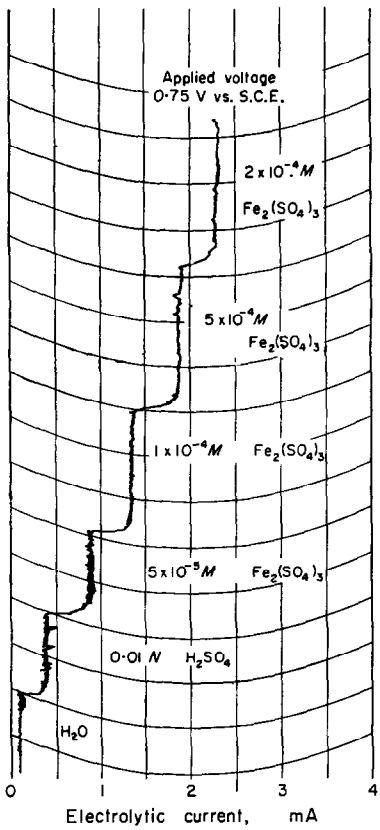


FIG. 7.—Record of continuous coulometric titrations of iron^{III} ion.

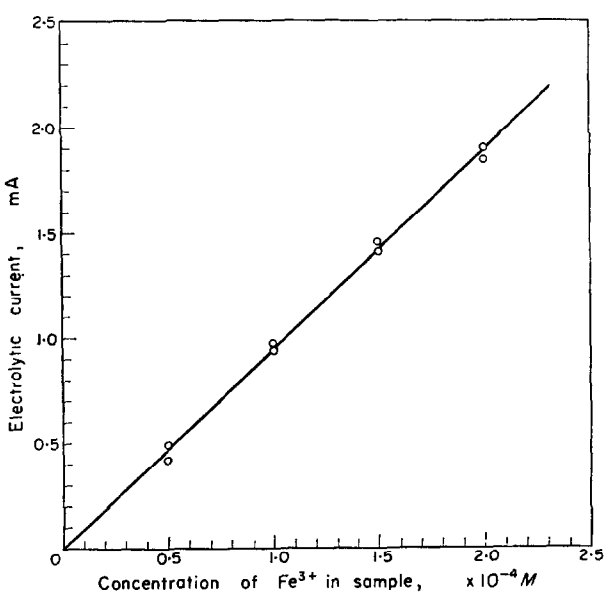


FIG. 8.—Relationship between concentration of iron^{III} ion in sample solution and electrolytic current.

Continuous coulometric titration of iron^{III}

The operation consists of two stages; the first is the reduction of iron^{III} in the sample solution by passage through the Jones' reductor (0·2 ml per sec) and the other is the continuous coulometric titration of the reduced solution flowing at 0·16 ml per sec from the small tank, C, shown in Fig. 2. The tank provides a constant head for the solution being titrated; unused solution is removed by suction. The electrolytic solution for electrogeneration of bromine flows at 0·1 ~ 0·2 ml per sec and an applied voltage of 0·73 ~ 0·75 V *vs.* S.C.E. is used. The electrolytic current is recorded on the chart of the recording milliammeter. An example of a run obtained is given in Fig. 7. At the change of a run of the sample solution, the recording gives a response lag of about 1 min, but the continuous method seems to be satisfactory for the analysis of the minute amounts of iron in water. The linear relationship between the concentration of iron^{III} and electrolytic current is shown in Fig. 8.

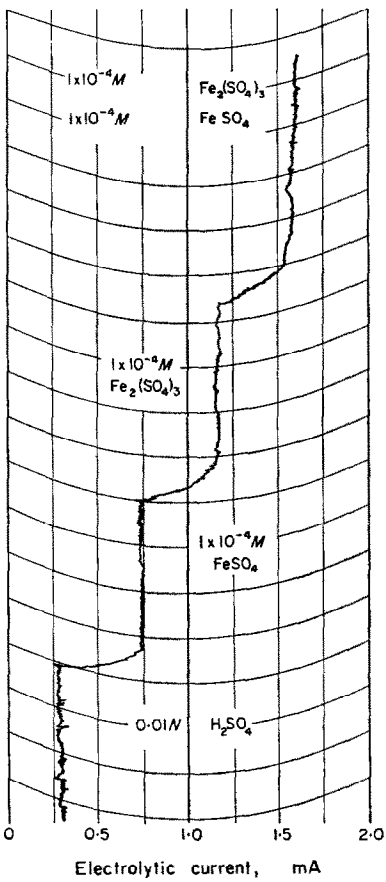


FIG. 9.—Record of continuous coulometric titrations of iron^{II} ion, iron^{III} ion and iron^{II} ion–iron^{III} ion.

Continuous coulometric titration of iron^{III} and iron^{II}

If the solution containing iron^{III} and iron^{II} is passed through the Jones' reductor, the total iron will be determined from the reduced solution. Fig. 9 shows an example of the charts recording the three kinds of sample solutions, containing respectively only iron^{II}, only iron^{III}, or both iron^{III} and iron^{II} ions. Table II summarises results obtained on the different sample solutions when they were allowed to flow for 10 min at 0·16 ml per sec with the applied voltage at 0·73 ~ 0·75 V *vs.* S.C.E. The experiment was continued for about 10 days, the electrolytic current values given in Table II being obtained by subtracting the background current which varied from day to day.

The variations seen in Table II might be caused by a number of factors such as differences in stirring, variations in sensitivity of the indicator electrode as well as the relative slowness of the reaction velocity between bromine and iron^{II}. The authors believe that if the experiments could be carried out without any breaks, even during the night, the results would be less prone to fluctuations.

Zusammenfassung—Es wird die continuierliche Bestimmung von Mikro-mengen von Eisen in wässriger Lösung mittels coulometrischen Titration mit Brom untersucht. Die Probe-lösung strömt continuierlich durch eine Jones' sche Reduktor darin Eisen zu Eisen^{II} reduziert wird, und coulometrisch mit Brom bestimmt wird. Die elektrolytische Lösung erhält Kalium-bromid in einer Puffer-lösung von Essigsäure-Natrium-acetat. Der End-punkt wird potentiometrisch ermittelt. Die Beziehung zwischen Eisen-mengen und elektrolytischen Ström ist zu etwa 15% proportional.

Résumé—Les auteurs ont mis au point le dosage en continu de microquantités de fer dans l'eau par titrage coulométrique avec du brome préparé par électrolyse. On fait circuler de manière continue la solution à travers un réducteur de Jones, le fer est transformé en fer ferreux et dosé par coulométrie par du brome. La solution électrolytique contenait du bromure de potassium temponné avec le mélange acide acétique-acétate de sodium, le point équivalent était déterminé par potentiométrie avec des électrodes platine-calomel. Dans des conditions convenables, il existe une relation de proportionnalité valable à 10% près entre le courant et la quantité de fer.

REFERENCES

[1] T. Takahashi and H. Sakurai, *Talanta*, 1960, **5**, 205.
[2] *Idem, J. Electroanalytical Chem.* in press.
[3] *Idem, ibid.*, in press.

Talanta, 1962, Vol. 9, pp. 205 to 211. Pergamon Press Ltd. Printed in Northern Ireland

A POLAROGRAPHIC STUDY OF DISSOLVED OXYGEN—I

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Summary—A polarographic study of dissolved oxygen has been carried out. Results obtained for reduction at the dropping mercury electrode indicate a disproportionation of one of the reaction products. The diffusion coefficient of oxygen in potassium chloride solution is calculated from the polarographic data.

FROM a consideration of the fundamental postulates of the theory of current-voltage curves at a polarisable electrode it has been shown by Ilkovic[1] that, for a process at the dropping mercury electrode which is truly diffusion controlled, a linear relation between the concentration of depolariser and of the limiting current produced by its reduction is to be expected. This has been confirmed for many substances over a wide concentration range. When it is established that a given reduction at the dropping mercury electrode is diffusion controlled, then other data concerning the reaction can be deduced from the curves obtained.

Thus, it is of importance to determine the ratio of depolariser concentration to limiting diffusion current over the concentration range of interest and this was, therefore, one of the first investigations undertaken.

Measurement of the diffusion current of the two oxygen waves was made over a range of dissolved oxygen concentration from 0·1 to 10 ppm. The base electrolyte used was 0·1*N* potassium chloride solution, the drop time was usually 3·6 sec and the potential sweep was from 0·0 to −0·5 V or from 0·0 to −1·7 V *vs.* the saturated calomel electrode.

Measurements of the diffusion current were made with due allowance for the residual current in each case. With nearly all series of measurements a check was made of the actual residual current (as distinct from the extrapolated one) by blowing out the oxygen in solution, then rescanning the same voltage range.

Using these techniques it was established that a linear relationship existed between oxygen concentration and limiting diffusion current over the range studied.

Measurements were carried out on both reduction waves. Since both reductions are two-electron processes, it would be expected that, as has been stated by many authors,[2,3,11] the two waves would be of equal height. It was noticed in this work, however, that although both the first and second reduction waves gave linear plots of limiting diffusion current against dissolved oxygen concentration the slopes were unequal, that for the first wave being equivalent to 0·229 μA/ppm while that for the

second was only 0·200 μA/ppm (Figs. 1 and 2). This difference in slope means that while the currents of the two waves are almost equal at low oxygen concentrations, at values near oxygen saturation the first wave is about 40% greater than the second.

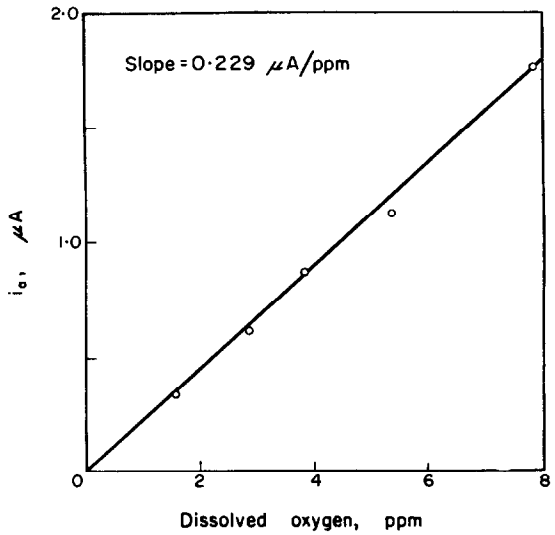


FIG. 1.—Plot of diffusion current against dissolved oxygen concentration for the first reduction wave of oxygen.

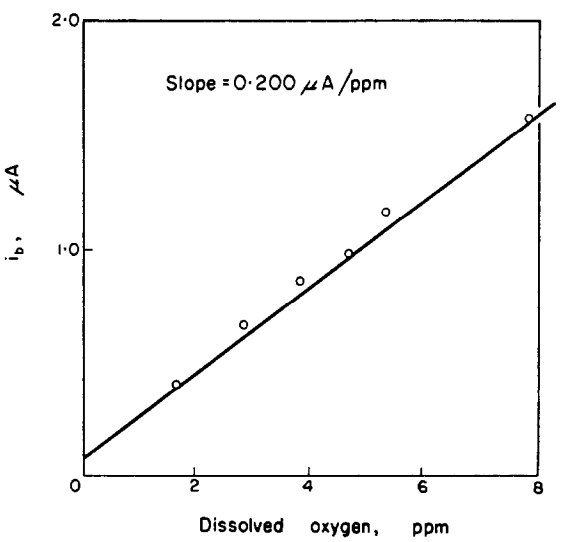


FIG. 2.—Plot of diffusion current against dissolved oxygen concentration for the second reduction wave of oxygen.

Since the second wave, from the reduction of hydrogen peroxide,[2,3] always appears smaller than the first one, a possible explanation which suggests itself is that of catalytic decomposition of the peroxide at the mercury surface before the reduction to water or hydroxyl ion takes place. This would seem to be in agreement with the increased difference between the waves at higher dissolved oxygen values. It would appear unlikely, however, that such a catalytic effect would be very reproducible,

especially if several different batches of mercury are used, as happened during the course of this work, nor would it be expected that a plot of total current of both waves against dissolved oxygen would be linear, although this is found in practice (Fig 3).

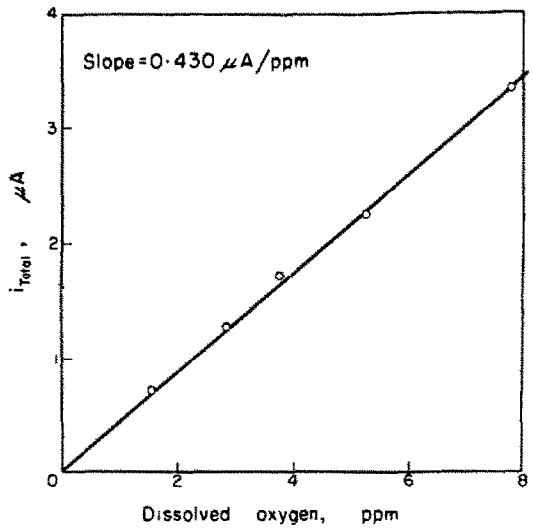


FIG. 3.—Plot of total limiting diffusion current against dissolved oxygen concentration.

A more probable reason for the changing ratio between the wave heights lies in a disproportionation reaction of the hydrogen peroxide. This type of reaction has been observed at very high concentrations (comparatively) of hydrogen peroxide by Giguere and Jaillet[4] who, however, state that this only occurs to any appreciable extent in solutions of hydrogen peroxide above 45 mM, while the concentrations involved in the present work are between one tenth and one hundredth of this.

If, however, we consider the first stage reduction of oxygen at the dropping mercury electrode:

$$O_2 + 2H^+ + 2e \rightarrow H_2O_2 \qquad (I)$$

then the limiting diffusion current i_A is proportional to the concentration of dissolved oxygen (O_2) [Found experimentally (Fig. 1) and agrees with the Ilkovic equation].

If a disproportionation reaction occurs:

$$2H_2O_2 \rightarrow O_2^* + 2H_2O \qquad (II)$$

then this oxygen O_2^* will also give rise to a reduction current i_A^*

Thus the total first stage diffusion current i_a will be the sum of these two:

$$i_a = i_A + i_A^*.$$

Since i_A^* is proportional to O_2^* and by (I) and (II) to the original concentration (O_2) then the gain in diffusion current (i_A^*) above that expected (i_A) at any given oxygen concentration should increase as the magnitude of this concentration increases. This is in agreement with the experimental facts quoted previously.

Now consider the overall reduction of oxygen to water at the dropping mercury electrode:

$$O_2 + 4H^* + 4e \rightarrow 2\,H_2O.$$

For this reaction the total diffusion current i_T should, by the Ilkovic equation, be proportional to the oxygen concentration O_2. This is found to be the case (Fig. 3).

At any concentration of dissolved oxygen, however, we have:

$$i_T = i_a + i_b$$

(where i_b corresponds to $H_2O_2 + 2e + 2H^* \rightarrow 2\,H_2O$)

Thus if i_a increases above that directly equivalent to (O_2) for the first stage reduction, then i_b should decrease.

This is just what is found experimentally, and hence it would appear that a probable explanation for the non-equality of the two reduction currents lies in the occurrence of a disproportionation reaction.

It is of interest to compare this suggested reaction with a mechanism proposed by Kolthoff and Jordan[5] for the reduction of hydrogen peroxide at a gold electrode. These authors suggest that the reduction of an oxygen molecule occurs according to:

$$O_2 + e \rightarrow O_2^-.$$

Further reduction then takes place with the final formation of hydrogen peroxide

$$O_2^- + e \rightarrow O_2^{2-}$$

$$O_2^{2-} + 2\,H^+ \rightarrow H_2O_2.$$

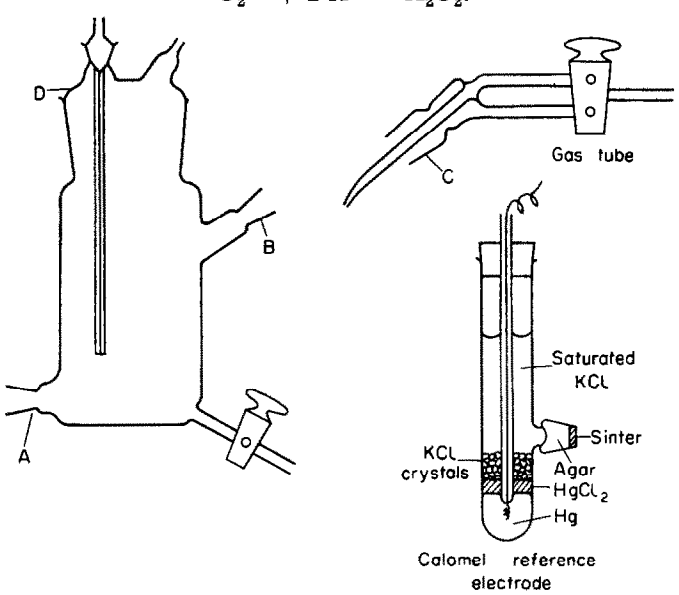


FIG. 4.—Cell used in preliminary experiments.

The O_2^- ion then reacts with a molecule of hydrogen peroxide:

$$O_2^- + H_2O_2 \rightarrow OH^- + O_2 + OH.$$

Longmuir[6], however, has suggested that his coulometric studies show that the overall reaction is not stoichiometric and that the number of Faradays passed per gram-molecule of oxygen reduced might vary with the initial oxygen concentration and thus that the relation between diffusion current and oxygen concentration would not produce a linear plot.

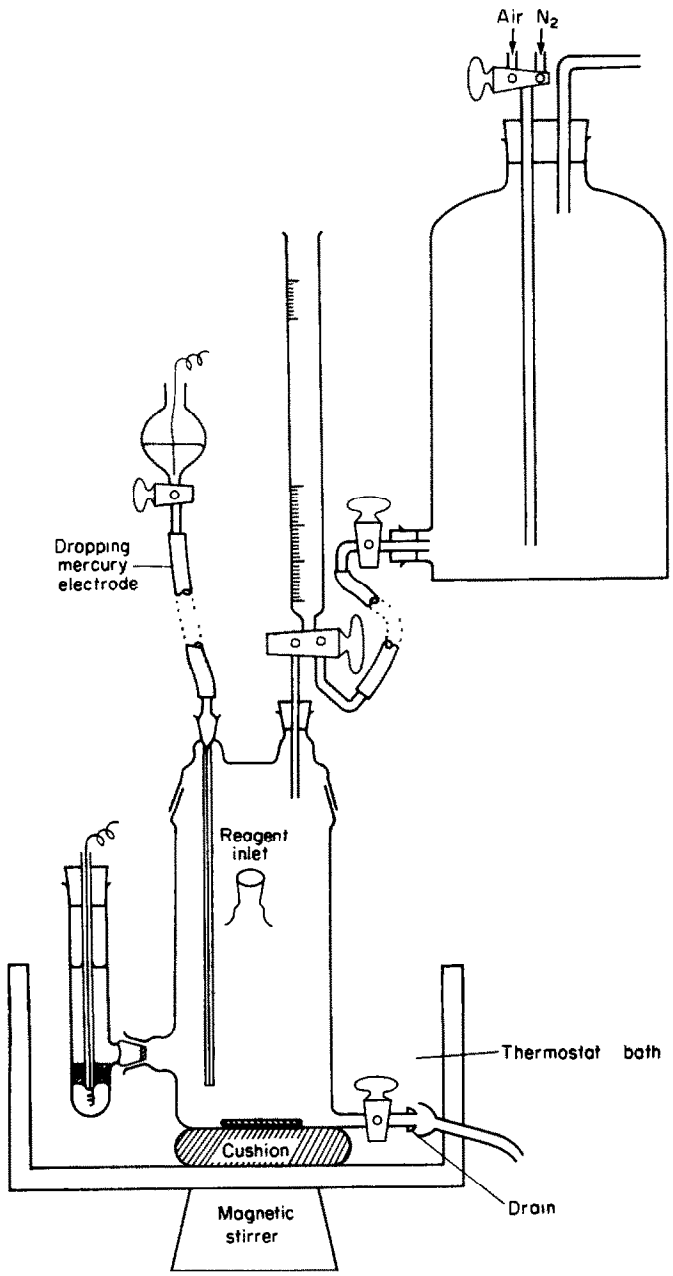


FIG. 5.—Cell used in more exact work with provision for preparation of solutions containing oxygen.

Since these present studies show, however, that the reduction at the dropping mercury electrode does give a linear plot, it is possible to calculate a value for the diffusion coefficient of oxygen (D) in 0·1*N* potassium chloride solution.

Taking the overall reduction of oxygen to water:

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \qquad \text{(i)}$$

and using the value of 0·430 μA/ppm for the total current (corresponding to i) from Fig. 3, we obtain a value for D at 20° of 1·609 $\times$ 10^{-5} cm^2/sec.

Few figures for the value of D in potassium chloride appear to be available in the literature, the value 1·86 $\times$ 10^{-5} cm^2/sec in pure water at 16° is given by Carlson and 1·98 $\times$ 10^{-5} cm^2/sec at 18° by Moelwyn-Hughes (both quoted by Wanner[7]), while *International Critical Tables* give a value of 8·1 $\times$ 10^{-5} sq ft/hr (*i.e.* 2·09 $\times$ 10^{-5} cm^2/sec) for pure water at 20°. Figures for the diffusion coefficient of oxygen in various buffers are given by Foffani and Vecchi[8] (1·92 $\times$ 10^{-5} cm^2/sec), Kern[9] (1·71 $\times$ 10^{-5} cm^2/sec for hydrogen peroxide) and Kolthoff and Laitinen[10] (2·38 $\times$ 10^5 cm^2/sec). The latter value was obtained at 25° using a platinium wire electrode. Foffani and Vecchi (*loc. cit*) also give a value of 2·02 $\times$ 10^{-5} cm^2/sec for the diffusion coefficient in potassium nitrate solution. This base electrolyte has also been used by Kolthoff and Miller[11] who obtain the high value of 2·6 $\times$ 10^- cm^2/sec. Arnold[12] gives a value of 2·00 cm^2/sec and quotes other references giving values from 1·54 – 2·2 cm^2/sec for the diffusion coefficient in water.

EXPERIMENTAL

During the preliminary experiments on this work the cell shown in Fig. 4 was used. This had a capacity of about 30 ml of solution and was fitted with a B16 standard socket A to take the reference electrode shown, a side arm B to take the gas tube and a B34 cone supporting a gas outlet and the dropping mercury electrode D.

By means of the gas tube a stream of nitrogen could be passed either through the solution for de-aeration or over its surface while measurements were being taken.

For the more exact work a cell was designed and made which could more easily be thermostatted and had provision for stirring. This latter was essential for the method used for the production of water containing a known amount of oxygen.

The method of obtaining standardised solutions of oxygen in the polarographic cell was to place a known volume of solution in the cell, de-aerate this and add a known volume of the same solution saturated with oxygen (Fig. 5). Since a reasonably large volume of air saturated solution could be prepared this could readily be standardised by the Winkler method as modified by Griffiths and Jackman[13] and Jackman.[14]

The polarograph used was a Tinsley Mark 15 D.C. Polarograph and the dropping mercury electrode used with a saturated calomel electrode as reference. All reagents were of AnalaR quality.

Zusammenfassung—Gelöster Sauerstoff wird studiert und es wird gefunden, dass eine Disproportionierungsreaktion stattfindet. Der Diffusionskoeffizient von Sauerstoff in Kaliumchloridlösung wird aus polarographischen Daten berechnet.

Résumé—Les auteurs ont fait une étude de l'oxygène dissous. Les résultats indiquent une réaction de dismutation. Le coefficient de diffusion de l'oxygène en solution de chlorure de potassium est calculé d'après les résultats polarographiques.

REFERENCES

[1] D. Ilkovic, *Coll. Czech. Chem. Comm.*, 1934, **6**, 498.
[2] G. W. C. Milner, *Principles and Applications of Polarography*. Longmans, Green & Co., 1957, p. 302.
[3] M. Brezina and P. Zuman, *Polarography*. Interscience Publishers Inc., 1958, p. 136.
[4] P. A. Giguere and J. B. Jaillet, *Canad. J. Res.*, 1948, **B16**, 767.
[5] I. M. Kolthoff and J. Jordan, *Analyt. Chem.*, 1952, **24**, 1071.
[6] I. S. Longmuir, *Biochem. J.*, 1954, **57**, 81.
[7] H. Wanner, *Helv. Chim. Acta*, 1945, **28**, 23.
[8] A. Foffani and E. Vecchi, Proc. 1st Intern. Polarog. Congress, Prague, 1922–50, Part 1, 64.
[9] D. M. H. Kern, *J. Amer. Chem. Soc.*, 1954, **76**, 4208.

[10] I. M. Kolthoff and H. A. Laitinen, *Science*, 1940, **92**, 152.
[11] I. M. Kolthoff and C. S. Miller, *J. Amer. Chem. Soc.*, 1941, **63**, 1013.
[12] J. H. Arnold, *ibid.*, 1930, **52**, 3937.
[13] V. S. Griffiths and M. I. Jackman, *Analyt. Chim. Acta*, 1957, **17**, 603.
[14] M. I. Jackman, Ph. D. Thesis, University of London, 1959.

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ACTIVATION ANALYSIS OF MOLYBDENUM IN PLANT MATERIAL

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Summary—The determination of molybdenum in plant material by means of activation analysis is described. Both activation to Mo^{99} ($t_{1/2}$ = 66 hr) and to Mo^{101} ($t_{1/2}$ = 14·6 min) is used. With the latter method the whole analysis takes about 1 hr. The extraction of molybdenum is carried out from a sulphuric acid medium using tri-*n*-octylamine in kerosene. The analysis has been performed on clover (*trifolium sp.*) and the results are in good agreement with those obtained by colorimetry using the thiocyanate method.

INTRODUCTION

MOLYBDENUM can be determined by neutron-activation analysis in two ways:

(1) $Mo^{98}(n,\gamma)Mo^{99} \xrightarrow[66\,hr]{\beta^-} Tc^{99} \xrightarrow[6\,hr]{\beta^-} Ru^{99}$ (stable)

$\sigma = 0{\cdot}45$ barns
$\theta = 23{\cdot}8\%$

(2) $Mo^{100}(n,\gamma)Mo^{101} \xrightarrow[14{\cdot}6\,min]{\beta^-} Tc^{101} \xrightarrow[14\,min]{\beta^-} Ru^{101}$ (stable)

$\sigma = 0{\cdot}20$ barns
$\theta = 9{\cdot}5\%$

The decay-scheme of Mo^{99} is reported in the literature.[1]

Bowen,[2,3] using the first method, irradiated biological samples for 3 days, followed by cooling periods of 6–72 hr. The molybdenum, separated by extraction with ether from 6*N* hydrochloric acid, was purified by precipitation of molybdenum α-benzoin-oximate. The separation took about 4 hr for 8 samples and the yield was 50 to 70%. A modified procedure, based on precipitation with α-benzoinoxime, was investigated by Decat and Roderbourg.[9]

A more rapid method, according to reaction (2), is described by Maddock and Meinke[4] who separated the Tc^{101} daughter product of Mo^{101}, by extraction with tetraphenylarsonium chloride. The irradiation takes 15 min and the analysis 1 hr.

The present work deals with the selective extraction of molybdenum from destroyed plant material, in a sulphuric acid medium, with tri-*n*-octylamine in kerosene, as first described by Brown *et al.*[5] Because the molybdenum content of the samples was of the order of 1 ppm, it was possible to check the results, obtained by activation analysis, by spectrophotometry according to a procedure described by Sandell.[6]

ACTIVATION AND MEASUREMENTS

Calculations show that reaction (1) gives 48·4 disintegrations/sec of Mo^{99} after irradiation of 1 μg of molybdenum for 5 hr in a slow neutron flux of $1{\cdot}4 \times 10^{12}$ $n.cm^{-2}.sec^{-1}$, the maximum flux in BR 1, whereas reaction (2) gives rise to 101

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† The untimely death of Mr. Leliaert occurred during the course of this study.

disintegrations/sec of Mo^{101} at the end of an irradiation of 1 μg of molybdenum for 20 min at this flux. When the time needed for the chemical separation is about 30 min, the activity of Mo^{101} decreases to 25 disintegrations/sec. Although the sensitivity for the molybdenum determination is higher when one activates to Mo^{99}, the time needed for the whole experiment is much longer. The measurements were made by means of a TMC* 256 channel analyzer connected to a 3″ × 3″ NaI(Tl) well-type detector. Mo^{99} is measured at the 140 keV line and Mo^{101} at the 191 keV line.

Preliminary experimental results showed that technetium is not extracted with tri-*n*-octylamine. Nevertheless Mo^{101} can also be determined using the 307 keV line of the Tc^{101} daughter activity after it has grown in the extract. Because Tc^{101} is in transient equilibrium with Mo^{101}, it is recommended in this case to wait about 15 min after separation in order to get maximum growth of Tc^{101}. If one measures between 15 and 30 min after extraction, the Tc^{101} activity is about constant and nearly the same as the Mo^{101} activity immediately after separation.

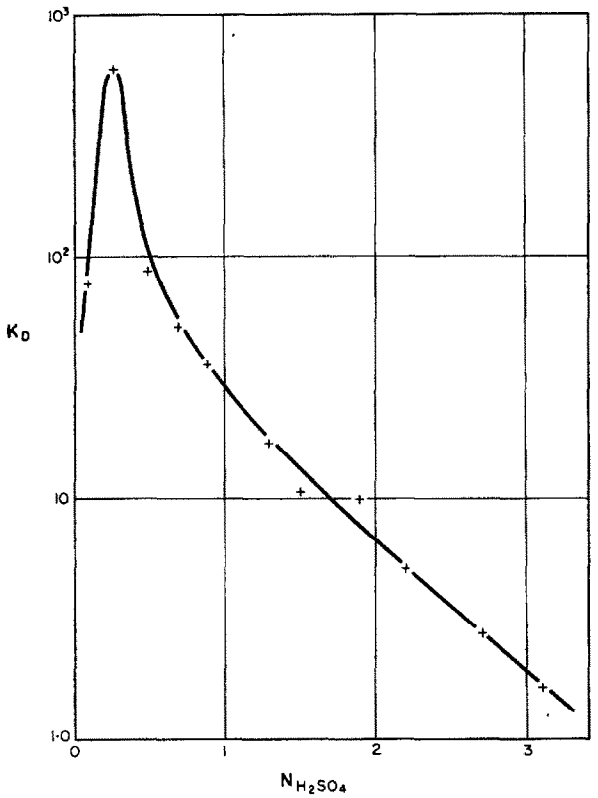


FIG. 1.—Distribution constant versus normality of sulphuric acid for molybdenum after extraction with a solution containing 2·5 v/v% of TOA in kerosene.

However, because the Tc^{101} activity is a rather complex function of time, it is practically impossible to check the half life of Tc^{101} and to correct for time differences between measurements. Although Tc^{101} measurement gives better statistics than the Mo^{101} measurement, it was preferred in view of the above mentioned reasons and the

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fact that in the case of Tc^{101} measurement it is necessary to treat sample and standard in the same way, to determine the Mo^{101} activity on the 191 keV line. Further, the whole analysis can now be carried out by one person, because the standard does not have to be extracted.

EXPERIMENTAL

Extraction of Molybdenum with Tri-n-octylamine in Kerosene

In this study the extraction of molybdenum[VI] from a sulphuric acid medium with tri-*n*-octylamine in kerosene was examined.[5] To 10 ml of sulphuric acid solution in a separatory funnel was added 1 ml of molybdenum solution containing 3 mg of molybdenum/ml as Na_2MoO_4 and 1 ml of Mo^{99}-tracer solution. After shaking for 1 min with 5 ml of a 2·5 v/v% solution of tri-*n*-octylamine in petroleum ether (b.p. 100–120°), the layers were allowed to separate and aliquots of both phases were taken for counting. Fig. 1 shows the results: distribution constant (K_D) versus normality of the sulphuric acid.

The normality of the sulphuric acid solution after extraction was determined by titration of an aliquot of the aqueous layer with 0·1*N* sodium hydroxide solution. From Fig. 1 it can be calculated that 96 ± 3% of the molybdenum is extracted for

$$0{\cdot}1N < N_{H_2SO_4} < 1{\cdot}0N.$$

Activation Analysis

Reagents

Sample: Approximately 0·5 g of clover (air-dried).
Standard: About 4 μg of molybdenum in a sealed quartz tube.
Carrier: Molybdenum trioxide.
Destructive agent: Perchloric acid (70%) and nitric acid (sp. gr. 1·4) mixed in equal volumes.
TOA solution: 2·5 v/v% solution of tri-*n*-octylamine in petroleum ether (b.p. 100–120°).
Lymphan indicator paper L 650: pH 0·4–1·4.
Conc. sulphuric acid
Sodium hydroxide: 4*N* and 2*N* solutions.

Mo^{101}

In a Plexiglass can, a sample and a standard are irradiated simultaneously for 20 min at a thermal flux of $1{\cdot}4 \times 10^{13}$ n.cm^{-2}.sec^{-1}. Immediately after irradiation, about 15 mg of carrier is added to the sample and this is heated with 4 ml of conc. sulphuric acid until fumes of sulphuric acid escape. The organic material is destroyed by adding dropwise about 5 ml of destructive agent. The resulting yellowish solution is heated again to expel the nitric and perchloric acids. After cooling for 2 min, 20 ml of water are added. When the solution is neutralised with 4*N* sodium hydroxide solution to pH 0·7–0·9 (about 0·7*N*), a slight precipitation of calcium sulphate occurs. After filtration through glass wool, the solution (approx. 40 ml) is extracted with 25·0 ml of TOA solution by mixing for 1 min. The phases are allowed to separate for 3 min and 20·0 ml of the organic layer are pipetted for measurement. When small volumes are concerned, the filtration step may be omitted.

Meanwhile the standard is dissolved in 25·0 ml of 2*N* sodium hydroxide solution and exactly 20·0 ml are counted.

The whole chemical separation takes about 15 min. About 10 min after irradiation, the standard is measured, then the sample and again the standard. Countings are made during a period of 10–13 min. Corrections are made for the decay of Mo^{101} in the sample versus the standard.

Mo^{99}

These analyses are made in nearly the same way. After neutron irradiation for 5 hr and a cooling period of 20 hr, the chemical separation is carried out.

Colorimetric Determination

This is carried out on samples of 2 g of clover according to the procedure described by Sandell.[6] The plant material is destroyed with sulphuric–nitric–perchloric acid. After destruction, all perchloric acid is expelled by heating to fumes of sulphuric acid. The solution is cooled, then boiled with 5 ml

of water to destroy any nitrosyl sulphuric acid. The sulphuric acid is neutralised with ammonia solution and 5 ml of 6*N* hydrochloric acid is added, followed by 2 ml of 5% sodium fluoride solution and 1 ml of 0·1% iron^{II} sulphate solution.

After filtration into a separatory funnel, the solution is diluted to 30 ml, then 4 ml of 20% potassium thiocyanate solution and 2 ml of 40% tin^{II} chloride solution in 1·5*N* hydrochloric acid are added with mixing. The molybdenum is extracted with 5 ml of a mixture of amyl alcohol and carbon tetrachloride (1:1 by volume). The phases are allowed to separate for 10 min and, after filtration of the organic layer through cotton, the absorption of the clear extract is measured at 465 mμ against water or another suitable blank (measurements were made on a Beckman spectrophotometer model B, in our case).

RESULTS

The above-mentioned procedures were applied to clover (*trifolium sp.*) and the results are summarised in Table I.

TABLE I—SUMMARY OF RESULTS

Method	Sample No.	Sample weight, *mg*	Mo found, μg	$N_{H_2SO_4}$ in aq. layer	Mo content, *ppm*	Devn. of the mean, %
Mo^{99}	1	759	0·744	0·74	0·98	1
	2	538	0·527	0·78	0·98	
	3	491	0·471	0·91	0·96	
Mo^{101}	4	442	0·427	0·77	0·97	4
	5	550	0·476	0·77	0·87	
	6	585	0·564	1·00	0·97	
	7	531	0·510	0·68	0·96	
	8	658	0·578	0·78	0·88	
	9	491	0·454	0·81	0·93	
Colorimetry	10	2000	1·87	—	0·93	2
	11	1998	1·96	—	0·98	
	12	1999	1·96	—	0·98	

As can be seen from Table I, the results obtained by different methods are in fairly good agreement. The method of Covell[7] was used for data evaluation of the gamma-ray spectra of Mo^{99} and Mo^{101}. In the case of Mo^{101}, the coefficient of variation, by this method, was 4%. Other evaluation methods of the gamma-ray spectral data gave coefficients of variation between 8% and 20%, although the same mean value was obtained. The main error is introduced by the subtraction of the Compton contribution of the 307 keV line of Tc^{101} from the Mo^{101} 191 keV line (see Fig. 2).

Under the experimental conditions used, the detection limit for the Mo^{101} method seems to be 0·1 μg, with a standard error of 35%. The recovery of molybdenum has been deduced by measurement of the acidity of the aqueous phase after extraction and by reference to the graph of distribution constant *vs.* normality of sulphuric acid (Fig. 1). The aqueous layer was always lower than 1*N* in sulphuric acid. From column 5 in Table I, it is seen that the pH adjustment can be made fairly well by the use of Lymphan indicator paper L 650.

Errors caused by $Ru^{104}(n,\alpha)Mo^{101}$ and $Ru^{102}(n,\alpha)Mo^{99}$ are not important, because of the low abundance of ruthenium in the samples and the low cross-sections for these

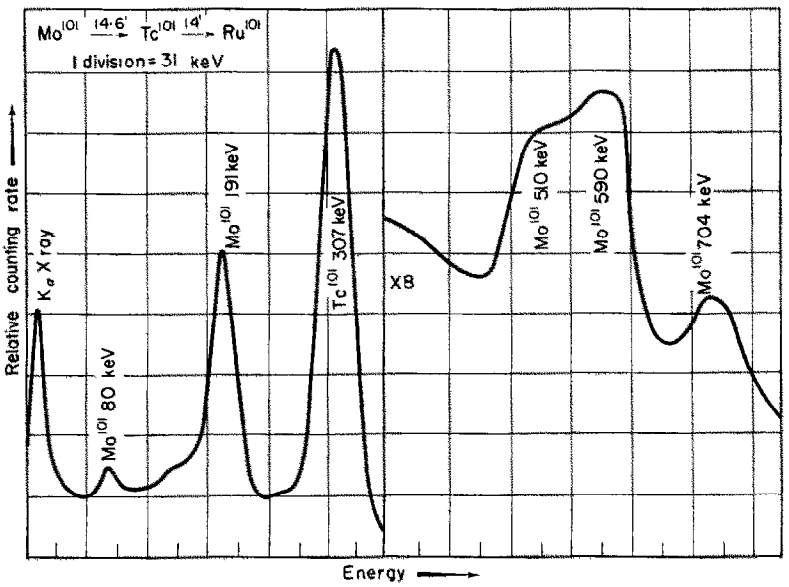


FIG. 2.—γ-Spectrum of a molybdenum standard obtained with a TMC 256 channel analyzer in a 3″ × 3″ NaI(Tl) well-type crystal (measurement made 10 min after irradiation for 10 min).

reactions. In the chemical treatment of the sample, uranium is co-extracted. Because the uranium content was lower than 50 ppb, no interference was introduced by the fission reaction $U^{235}(n,f)Mo^{101}$, Mo^{99}. The 74 keV line of U^{239} ($t_{1/2}$: 23·5 min) has no effect on the measurement of Mo^{101}.

A description of the determination of uranium based on the same extraction procedure will be published soon.[8]

Zusammenfassung—Die Bestimmung von Mo im Pflanzenmaterial mittels Aktivierungsanalyse wird beschrieben. Mo^{99} ($t_{1/2}$ = 66 h) und Mo^{101} ($t_{1/2}$ = 14,6 min) wurden herangezogen. Mit der letzteren Methode benötigt die gesamte Analyse ungefähr eine Stunde. Die Extraktion des Mo wird aus schwefelsäurer Lösung mit Tri-n-octylamin in Kerosin bewerkstelligt. Die Analyse wurde auf Klee (Trifolium sp.) angewandt und die erhaltenen Resultate stehen in gutem Einklang mit denen auf kolorimetrischem Wege (Thiocyanatmethode) erzielten.

Résumé—La détermination du molybdène dans les matériaux végétaux au moyen d'analyse par activation a été mise au point. L'activation au Mo^{99} ($t_{1/2}$: 66 h) aussi bien qu'au Mo^{101} ($t_{1/2}$: 14,6 m) a été employée. La durée de l'analyse totale par la dernière méthode est d'environ une heure. Le molybdène est extrait à partir d'un milieu acide sulfurique par la tri-n-octylamine. La détermination a été effectuée sur du trèfle, et les résultats sont en bon accord avec ceux obtenus par colorimétrie.

REFERENCES

[1] D. Strominger, J. M. Hollander and G. T. Seaborg, *Rev. Mod. Phys.*, 1958, **30**, 670.
[2] H. J. M. Bowen, *Intern. J. Appl. Radiation and Isotopes*, 1959, **5**, 227.
[3] H. J. M. Bowen and P. A. Cawse, AERE-R-2925 (1959), Nuclear Sc. Abstr., 1959, **13**, ref. 14216.
[4] R. S. Maddock and W. W. Meinke, *Univ. of Michigan, Prog. Rep.*, 1958 (Nov.)–1959 (Oct.), **8**, 77.
[5] K. B. Brown, C. F. Coleman, D. J. Crouse, J. O. Denis and J. G. Moore, Report ORNL-1734, see G. H. Morrison and M. Freiser, *Solvent Extraction in Analytical Chemistry*. John Wiley and Sons Inc., New York. 1957, p. 219.
[6] E. B. Sandell, *Colorimetric Determination of Traces of Metals*. Interscience Publishers Inc., New York, 1959. p. 644–663.

[7] D. F. Covell, USNRDL-TR-288 (1958), *Analyt. Chem.*, 1959, **31**, 1785.
[8] D. Decat, B. van Zanten and G. Leliaert, Symposium on Activation Analysis, Grenoble, 1961.
[9] D. Decat and Roderbourg, unpublished results.

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A SCHEME FOR THE RAPID ANALYSIS OF URANIUM-ORE ACID LEACH SOLUTIONS

DETERMINATION OF ALUMINIUM, ARSENIC, CALCIUM, CADMIUM, COBALT, COPPER, MAGNESIUM, NICKEL, AND ZINC IN PRESENCE OF EXCESS IRON AND MANGANESE

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Summary—A scheme for the rapid quantitative analysis of uranium-ore acid leach solutions or solutions of similar composition is described. As, Cd, Co, Cu, Ni and Zn are determined polarographically, tions of similar composition is described. As, Cd, Cu, Co, Ni and Zn are determined polarographically, for the separation of Al, Cd, Ca, Co, Mg and Zn from Fe and Mn and from each other by anion-exchange chromatography and solvent extraction of oxinates.

IN the course of work on effluents from uranium mines a need arose for quantitative determination of aluminium, arsenic, calcium, cadmium, cobalt, copper, iron, magnesium, manganese, nickel and zinc in "pregnant" solutions (relatively rich in uranium, ready to be processed on ion-exchange columns) and in "barren" solutions (column effluents, which are practically devoid of uranium).

Both solutions contain a few elements, such as iron and manganese, in considerable amounts, and a number of other elements in trace or near trace quantities. Interferences in analysis for these trace elements are, therefore, to be expected, and elaborate and time-consuming separations would normally be required in order to determine them. The literature search for an integrated scheme of analysis for the above elements in solutions of similar composition proved unfruitful. The aim of this work was to evolve such a scheme, the emphasis being on rapidity and simplicity. In addition to the selection and adaption of suitable methods of analysis, this involved the development of a method for the separation of Al, Ca, Cd, Co, Mg and Zn from iron and manganese and from each other by anion-exchange chromatography and solvent extraction of oxinates.

Iron and manganese were determined directly, without prior separation. Iron was determined colorimetrically with 1,10-phenanthroline.[17] Although barren and pregnant solutions contained interfering ions,[13,17] their ratio to that of iron was so small that they constituted no source of error. This method is more convenient than the titrimetric potassium dichromate method[2,10] and results are comparable (Table II). Manganese was also determined colorimetrically,[14] measuring at 525 mμ in the spectrophotometer the permanganate colour developed with potassium periodate. If the sample was well boiled with nitric acid to remove any easily oxidisable matter present, preliminary fuming with sulphuric acid and oxidation with ammonium persulphate were unnecessary.[9]

Copper and nickel were determined simultaneously by polarography, using pyridine-

hydrochloride as the base electrolyte.[11] This base electrolyte precipitated interfering elements, which were removed by filtration. Hitchin[6] used this method for determination of Cu, Ni and Co in cobalt concentrates and in solutions containing uranium. However, South African barren and pregnant solutions contain zinc, which has a polarographic wave which coalesces with that of cobalt, and therefore preliminary separation of these two metals was necessary.

Arsenic was separated from interfering elements by a simple distillation,[5] and subsequently determined polarographically.[4]

A preliminary separation was necessary in the case of Al, Ca, Cd, Co, Mg, and Zn, and it was found that this separation could be very conveniently achieved by means of ion-exchange chromatography. Kraus and Nelson[7] studied the behaviour of many metals in hydrochloric acid solutions on strongly basic ion-exchange columns. It was clear from their work that a certain number of ions, such as those of Al, Ca, Mg, Ni and some other metals were not absorbed by the resin under selected conditions, and therefore could be collected as a separate fraction. Other ions were retained by the resin to a greater or lesser extent, and could be eluted separately and successively by changing the concentration or nature[16] of the eluting solvent. In this way it was possible to separate metals present in barren and pregnant solutions into four fractions containing (a) aluminium, calcium, magnesium, manganese and nickel; (b) cobalt; (c) most of the iron; (d) cadmium and zinc. The conditions for this separation are given in the experimental section of this paper, where it will be seen that the recovery of metals was quite satisfactory. Recently similar separations were reported by Wilkins[19,20] and Carson.[1]

Cobalt was then easily determined polarographically using the same base electrolyte as in the case of copper and nickel.[7] Zinc and cadmium were also determined by polarography, with ammonia-ammonium chloride as supporting electrolyte.[12] The concentration of zinc in these solutions was usually much higher than that of cadmium, and the particular fraction had to be diluted with base electrolyte before the polarogram for zinc could be recorded.

Although most of the interfering ions were removed by anion-exchange chromatography, nickel and manganese were still present in the fraction containing aluminium, calcium and magnesium. Aluminium was separated by extraction of its 8-hydroxyquinoline complex at pH 5 with chloroform, and determined by measuring spectrophotometrically at 395 mμ the intensity of the yellow colour formed.[15] In this procedure nickel oxinate is also extracted into chloroform and interferes. It was found however, that in the case of S. African barren and pregnant solutions, where the concentration of nickel is at least ten times smaller than that of aluminium, the interference was negligible (Table III). The colour intensity should be measured without delay, in order to avoid decrease of absorbance from photochemical decomposition of the complex.[8]

Further extraction of the aqueous layer with 8-hydroxyquinoline in chloroform at pH 8 removed most of the manganese,[15] and calcium and magnesium were determined together by titration with ethylenediaminetetra-acetic acid in the presence of triethanolamine with Eriochrome Black T as indicator.[3,18]

The scheme of analysis showing the sequence of operations is given in Fig. 1. It will be seen from the analysis of a synthetic mixture (Table IV) that the accuracy and sensitivity of the methods used were satisfactory for the purposes of this work,

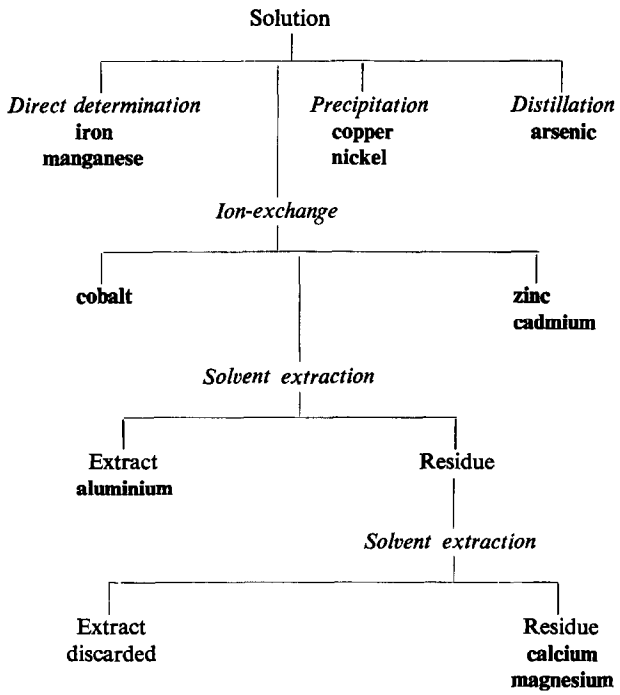


FIG. 1.—The scheme of analysis.

in which the emphasis was on speed and simplicity. There is no doubt that most of the methods of this scheme could be used in much more critical work, and the scheme itself applied to solutions other than those encountered in the uranium industry.

TABLE 1.—ANALYSIS OF URANIUM PREGNANT AND BARREN SOLUTIONS

Solution	Fe	Cu	Ni	Mn	As	Co	Cd	Zn	Al	Ca + Mg (as $CaCo_3$)
(A) Pregnant	3,260	20	28	3,250	41	16	0·24	77	508	2,730
Barren	3,220	16	26	3,500	40·5	17	0·29	44	504	2,850
(B) Pregnant	3,220	16	108	4,600	410	53	0·70	148	408	3,120
Barren	2,840	13	96	4,300	339	42	0·61	133	422	2,800
(C) Pregnant	5,360	29	32	3,400	76	33	0·83	86	1,284	4,070
Barren	5,240	24	30	3,280	69	36	0·90	73	1,336	5,250
(D) Pregnant	4,880	4·0	100	260	107	66	0·43	107	861	4,750
Barren	5,120	3·6	88	275	107	71	0·57	115	1,120	6,050
(E) Pregnant	3,180	12	50	8,050	107·5	34	0·49	110	690	4,200
Barren	2,910	12	46	7,700	100	28	0·26	68	740	2,950
(F) Pregnant	4,120	14	34	5,150	54·5	20	0·33	60	1,140	4,650
Barren	3,060	6	19	2,200	32·6	16	Trace	34	444	1,550

The results are expressed as mg/litre of metal.

In order to show the range of concentrations of different metals usually encountered in S. African barren and pregnant solutions, the results of analysis of solutions from six different uranium-producing mines are reproduced in Table I. In each case the solutions were analysed according to the described scheme.

EXPERIMENTAL

Apparatus and reagents

A K-1000 Cathode Ray Polarograph, Southern Instruments, Ltd., with a polarographic cell modified in such a way that it could accommodate a saturated calomel reference electrode (S.C.E.), and a Zeiss Spectrophotometer, Model PMQ II, were used. Analytical grade reagents were used.

Iron

A 10-ml aliquot of the sample solution is diluted to 1000 ml in a volumetric flask, adding 1 ml of hydrochloric acid to keep iron in solution, if necessary. A 5-ml portion of this solution is transferred into a 100-ml flask, 1 ml of hydroxylamine hydrochloride, 10 ml of 1,10-phenanthroline solution and 1 ml of sodium acetate buffer, prepared as in reference 17, are added, and the solution is made up to the mark with distilled water. The colour intensity is read against a reagent blank, at 508 mμ in the spectrophotometer, using a 1-cm cell.

The concentrations are read from a calibration curve.

The results obtained by this method are compared in Table II with those obtained by titration of iron with potassium dichromate.

TABLE II. COMPARISON OF IRON DETERMINATIONS BY 1,10-PHENANTHROLINE AND POTASSIUM DICHROMATE METHODS

Solution	1,10-phenanthroline, *ppm*	Potassium dichromate, *ppm*
Pregnant C	5360	5200
Pregnant E	3180	3120
Pregnant F	4120	4140
Barren C	5240	5150
Barren E	2910	2840
Barren F	3060	2950

Manganese

An aliquot (1–10 ml) of the solution is pipetted into a 500-ml squat beaker. To this 30 ml of conc. nitric acid are added and the solution is boiled for 10 min, then diluted to 200 ml with water and about 1 g of potassium periodate is added. The solution is boiled for 2–3 min, then kept warm for 30 min, to allow the colour to develop fully. After cooling, it is transferred to a 500-ml volumetric flask and made up to the mark. The colour intensity is read in a 1-cm cell against a distilled water blank at 525 mμ in the spectrophotometer.

The concentrations are read from a calibration curve.

Copper and nickel

To 25 ml of the solution in a 250-ml beaker, 3 ml of 12*M* hydrochloric acid and 5 ml of 16*M* nitric acid are added. The solution is boiled for 5 min, then evaporated to incipient dryness on a water-bath, and, after moistening with hydrochloric acid, evaporated to dryness to destroy the nitric acid. The residue is dissolved in 2 ml of 12*M* hydrochloric acid, transferred to a 100-ml volumetric flask, 5 ml of pyridine are added, and the solution is made up to the mark with distilled water. The precipitate is filtered off on Whatman No. 42 paper, an aliquot of the filtrate is transferred to the polarographic cell, and the polarogram is recorded at −0·39 V and −0·9 V *vs.* S.C.E. for copper and nickel, respectively.

The concentrations are read from calibration graphs.

Arsenic

A long-neck distillation flask of 200-ml capacity, fitted with a thermometer, a gas inlet tube for nitrogen dipping to the bottom of the flask, and an efficient condenser, are used for arsenic distillation. The distillate is collected in a ground-glass Friedrich gas-washing bottle of 100-ml capacity, cooled in an ice bath.

A 10-ml aliquot of the sample, 5 ml of reduction mixture (10% hydrazine hydrochloride and 7% potassium bromide), 5 ml of phosphoric acid and 70 ml of 12*M* hydrochloric acid are placed in the distillation flask, and 10 ml of distilled water in the receiving flask. The apparatus is assembled, a moderate stream of N_2, which prevents bumping and sucking back, is started, and about 70 ml of the distillate are collected in the cooled receiving flask (stop distillation when temperature reaches 115°). The distillate is washed into a 600-ml squat beaker, and about 30 ml of potassium hydroxide solution (60 g dissolved in 100 ml) are added with constant cooling, till the pH is between 0·15 and 0·20 units (pH meter). This solution is transferred to a 500-ml (if necessary 250-ml) volumetric flask and made up to the mark with distilled water. An aliquot of the solution is transferred to a polarographic cell, and the polarogram recorded at −0·47 V *vs.* S.C.E.

The arsenic concentration is obtained from a calibration graph.

Separation of Ca, Mg, Al, Co, Zn *and* Cd *by ion-exchange chromatography*

A strong base anion-exchange resin, Amberlite CG-400 Type 1, 100–200 mesh, chloride form, is used. The resin is packed as a slurry in distilled water, into a 1 × 40-cm glass column provided with a tap, to the height of 30 cm. The bed volume of such a column is 20–25 ml. After washing with 50 ml of 9*M* hydrochloric acid, the column is ready for use.

A 10 ml portion of barren or pregnant solution, to which 1 ml of 100-vol. H_2O_2 is added, is evaporated to dryness on a water-bath. The residue is dissolved in a minimum amount of 9*M* hydrochloric acid, and applied to the column in the usual way. The mixture of metal complexes is then eluted, at a flow rate of about 80 ml/hr, with:

(*a*) 50 ml of 9*M* HCl (two bed-volumes)
(*b*) 50 ml of 4*M* HCl
(*c*) 50 ml of 0·5*M* HCl
(*d*) 60 ml of 1*M* HNO_3

to give fractions (*a*), (*b*), (*c*) and (*d*), respectively, which are collected separately. Fraction (*c*) is discarded.

After washing with 50 ml of water and 50 ml of 9*M* hydrochloric acid, the column is again ready for use. Since strong HCl attacks the resin to a certain extent, the column is normally treated with 9*M* hydrochloric acid just before it is used.

Aluminium

Fraction (*a*) (from the separation by ion-exchange chromatography) is made up to 100 ml with distilled water, and a 10-ml aliquot is evaporated to dryness on a water-bath. The residue is dissolved in 1 ml of 1:4 hydrochloric acid, transferred to a 100-ml separating funnel, 10 ml of 10% sodium acetate solution are added, and the whole is diluted to about 40 ml with distilled water. (The pH of the solution must be 5). A 10-ml portion of 5% 8-hydroxyquinoline in chloroform is added, and the funnel is immediately stoppered and shaken for 1 min. After separation of the phases, the chloroform layer is run off into a dry 100-ml volumetric flask. This extraction is repeated twice more using 5 ml of 5% 8-hydroxyquinoline solution mixed with 5 ml of chloroform, and finally with 10 ml of pure chloroform. All extracts are combined. The extracted aqueous layer is kept for the determination of calcium and magnesium.

The chloroform extract is made up to 100 ml with pure chloroform, about 2 g of anhydrous sodium sulphate are added, and the flask is well shaken. An aliquot is decanted into a 1-cm cell, and the absorption against a blank of 1% 8-hydroxyquinoline in chloroform is read at 395 mμ in the spectrophotometer.

The aluminium concentration is obtained from a calibration graph.

The results of the determination of aluminium by the above method in the presence of manganese, calcium, magnesium and nickel are given in Table III, from which it will be noted that nickel does not interfere significantly when present in small amounts.

TABLE III.—DETERMINATION OF Al IN THE PRESENCE OF Mn, Ni, Ca AND Mg

Taken, *μg*					Found, *μg*
Al	Mn	Ni	Ca	Mg	Al
9	10	2·5	5	2	10·5
27	30	7·5	15	6	28·6
9		2·5			11·2
27		7·5			29·8
9	10		5	2	9·0
27	30		15	6	26·9
9		10			12·0
27		30			31·8
9		1			9·2
27		3			26·7

Calcium and magnesium

After extraction of aluminium, as described above, the extracted aqueous layer is transferred to a 200-ml beaker, and the pH of the solution is adjusted to 7·5–8·0 with 5% sodium hydroxide (pH meter). The solution is then transferred back to the separating funnel and extracted with 5% 8-hydroxyquinoline in chloroform, as directed for aluminium, but the chloroform layer is discarded. The extraction is repeated with 5 ml of 8-hydroxyquinoline and 5 ml of chloroform at least three times, or until the chloroform layer becomes colourless, and finally with 10 ml of pure chloroform.

The extracted aqueous layer is transferred ino a 100-ml porcelain dish, and 30 ml of 30% triethanolamine solution, 1 ml of ammonia buffer solution and a few drops of Eriochrome Black T indicator are added. The solution is titrated with standard 0·02*M* EDTA solution to a blue end-point. The results are expressed as ppm of $CaCO_3$.

Cobalt

Fraction (*b*) (from the separation by ion-exchange chromatography) is evaporated to dryness on a water-bath, and the residue is dissolved in 2 ml of 12*M* hydrochloric acid. The solution is then transferred to a 100-ml volumetric flask, 5 ml of pyridine are added, and the whole is made up to the mark. An aliquot is transferred to the polarographic cell and the polarogram is recorded at −1·15 V *vs.* S.C.E.

The concentration is read from a calibration graph.

TABLE IV.—ANALYSIS OF A SYNTHETIC MIXTURE

Metal	Taken, *ppm*	Found, *ppm*		
Fe	2000	1980, 2060		
Mn	2170	2180, 2200		
Cu	36	36, 37		
Ni	60	60, 60		
As	103	99, 103		
		Column 1	Column 2	Column 3
Zn	95	96	97	99
Cd	2·4	2·4	2·4	2·4
Co	25	24	24	27
Al	450	440	440	450
Ca + Mg (as $CaCO_3$)	3650	3600	3690	3630

Zinc and cadmium

Fraction (*d*) (from the separation by ion-exchange chromatography) is evaporated to dryness on a water-bath. The residue is dissolved in 2 ml of 1:1 hydrochloric acid, transferred carefully to a 10-ml volumetric flask and neutralised with ammonia. To it 0·5 g of ammonium chloride is added and the solution is made up to the mark with distilled water. An aliquot is transferred to the polarographic cell and the polarogram is recorded at −0·75 V and −1·30 V *vs.* S.C.E. for cadmium and zinc respectively.

The concentrations are read from calibration graphs.

Analysis of a synthetic mixture

A synthetic mixture, containing aluminium, arsenic, calcium, cadmium, cobalt, copper, iron, magnesium, manganese, nickel and zinc was analysed according to this scheme. The results are reproduced in Table IV.

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Zusammenfassung—Ein Schema zur raschen, quantitativen Analyse von sauren Auslaugungen von Uranerzen und ähnlichen Lösungen wird beschrieben. As, Cd, Co, Cu, Ni und Zn werden polarographisch erfasst, Al, Fe und Mn colorimetrisch und Ca und Mg durch ÄDTE-Titration. Eine Trennung von Al, Cd, Ca, Co, Mg und Zn von Fe und Mn sowie voneinander mittels Ionenaustauschchromatographie und Solvent-extraktion unter Verwednung von Oxin wird beschrieben.

Résumé—Les auteurs décrivent un schéma d'analyse quantitative rapide de solutions acides de mineral d'uranium ou de solutions de composition semblable. As, Cd, Co, Cu, Ni et Zn sont dosés par polarographie, Al, Fe et Mn par colorimétrie et Ca et Mg par titrage par l'EDTA. Le schéma comprend une méthode de séparation de Al, Cd, Ca, Co, Mg et Zn d'une part, et de Fe et Mn d'autre part, par chromatographie d'échange d'ions et extraction d'oxinates par un solvant.

REFERENCES

[1] R. Carson, *Analyst*, 1961, **86**, 198.
[2] G. Charlot and D. Bezier, *Analyse quantitative minerale*. Masson & Co., Paris, 3rd Edition, 1955. p. 527.
[3] H. J. Cluley, *Analyst*, 1954, **79**, 567.
[4] T. Hetman, *Trace Techniques*. Southern Instruments, Ltd., Camberley, Surrey, 1959. p. 14.
[5] W. F. Hillebrand, *Applied Inorganic Analysis*. Wiley, New York, 2nd Edition, 1953. p. 69.
[6] A. Hitchin, *Topical Report No. TR*117/54, Department of Mines and Technical Survey, Ottawa, Canada.
[7] K. A. Kraus and F. Nelson, *International Conference on the Peaceful Uses of Atomic Energy*, Geneva, 1955. Proceedings, **1**, 113.
[8] R. H. Linell and F. H. Raab, *Analyt. Chem.*, 1961, **33**, 154.
[9] Central Metallurgical Laboratory, Anglo American Corporation of South Africa, Ltd., private communication.
[10] *Idem*, private communication.
[11] G. W. C. Milner, *The Principle and Applications of Polarography*. Longmans, London, 1957. p. 331.
[12] C. J. Sambucetti, E. Witt and A. Gorri, *International Conference on the Peaceful Uses of Atomic Energy*, Geneva, 1955. Proceedings, **8**, 266.
[13] E. B. Sandell, *Colorimetric Determination of Traces of Metals*. Interscience, New York, 3rd Edition, 1959. p. 522.
[14] *Idem, ibid.*, p. 606.
[15] *Idem, ibid.*, p. 219.
[16] F. D. Snell, *Colorimetric Methods of Analysis*. Van Nostrand, New York, 1959, Vol. IIa. p. 92.
[17] *Standard Methods for the Examination of Water, Sewage and Industrial Wastes*. American Public Health Association, Inc., New York, 1955, 10th Edition. p. 124.
[18] F. J. Welcher, *The Analytical Uses of Ethylenediaminetetraacetic acid*. Van Nostrand, New York, 1959. p. 103.
[19] D. H. Wilkins, *Talanta*, 1959, **2**, 355.
[20] D. H. Wilkins and L. E. Hibbs, *Analyt. Chim. Acta*, 1959, **18**, 372.

Talanta, 1962, Vol. 9, pp. 227 to 237. Pergamon Press Ltd. Printed in Northern Ireland

ANALYSIS OF GASES AND VAPOURS BY SPECTROSCOPIC TECHNIQUES—II*

REVIEW OF THE ABSORPTION SPECTRA OF GASES AND VAPOURS

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Summary—The electronic molecular absorption of gases and vapours has been reviewed, particular emphasis being given to the spectra obtained from organic molecules.

THERE exists an exceedingly large volume of information on the electronic absorption spectra of organic compounds. The relationship between the nature of the absorption spectrum and the chemical constitution of organic compounds has been reviewed by Ferguson,[1] and the many aspects of electronic absorption spectroscopy are covered in the book by Gillam and Stern.[2]

Most absorption results have been obtained using a liquid phase, and this practice introduces a complex variable which may be called the "solvent effect". Comparison of the absorption properties of a substance in the vapour phase and in solution shows that dissolution damps down the molecular rotation and thus produces broad absorption bands where fine structure peaks can be observed in the spectra of the vapour phase. A similar transformation is noticeable when solutions of substances in non-polar and polar solvents are compared. A change of solvent can also induce changes in the intensity of an absorption band, and can cause a displacement of bands along the wavelength scale.

Apart from these physical "solvent" effects, a change of solvent may bring about a radical change in the nature of the absorption of a substance. This change can be caused by chemical interaction with the solvent; or by complex formation; or by dissociation; or by equilibration of two tautomers in solution.

The absorption spectra obtained using the vapour phase should theoretically be free of the many disadvantages introduced by "solvent effects" but little use appears to have been made of this approach. Admittedly the experimental technique for handling gases or vapours is more cumbersome than that required for work using solutions; but as a preliminary to surveying the analytical possibilities of this approach a review has been made of existing publications on the absorption of visible and ultra-violet radiation by gases and vapours.

THEORY OF ELECTRONIC ABSORPTION SPECTROSCOPY

It is proposed to adopt here the same procedure as that used in Part I of this series, *i.e.*, to give an outline of the theoretical principles directly concerned with analytical applications, and not to delve deeply into basic theory, which is covered by existing text books.[3,4]

* Part I: *Talanta*, 1961, **8**, 892.

Atomic line spectra

The atomic line spectrum of an element can be obtained in absorption if a sufficient concentration of free atoms can be maintained in the vapour phase in a given path length. For metals this necessitates vaporisation in a flame or an electric arc, and although it would seem in this case preferable and simpler to use the emission spectrum, recent work on atomic line absorption, using flame photometric techniques, has shown that the method possesses valuable analytical possibilities.[5]

Within the scope of this review, the only gases giving rise to such line spectra are those of Group O in the Periodic Table, *i.e.*, the inert gas group. As stated in Part I, the emission spectra of these gases lies principally in the visible and near ultraviolet and can be used for qualitative and quantitative analysis. Their absorption spectra however lie in the extreme vacuum ultraviolet, a region not readily accessible to routine spectroscopic equipment.

Since the emission spectrum of an inert gas is in the visible region, it would appear reasonable that the absorption spectrum should lie in the same region. This is not necessarily so, however. If we take neon as a typical example, it has six $2p$ electrons and the L_1 and L_2 shells are completely filled; this means that the ground electronic state is $1\ ^1S_0$. An excited state will result when an electron is moved from the L_2 shell to a higher orbital, but for neon, as for all inert gases, the energy required to do this is very large, because it involves a change in the principal quantum number. When only one electron is excited, we have the first excited state, which is also an S state, since the quantum number for orbital angular momentum, l, is zero. We now have two unpaired electrons, giving a total spin of 1 which means that this first excited state is $2\ ^3S$. (The multiplicity, *i.e.*, the suspercript to the term symbol is given by twice the total spin + 1.) The next excited state, when two electrons are excited and paired together with opposed spins in orbit 2, will by similar reasoning be 2^1S, since the total spin is now zero. Neither of these states will combine with the ground state, because $2\ ^3S \rightarrow 1\ ^1S_0$ would involve a change of multiplicity, which is forbidden, and for $2\ ^1S \rightarrow 1\ ^1S_0$ the selection rule $\Delta l = \pm 1$ is broken. Such metastable states cannot, therefore, be reached by absorption of radiation. The first excited state which does combine with the ground state is $2\ ^1P$, and the transition $2\ ^1P \rightarrow 1\ ^1S_0$ gives rise to absorption in the far ultraviolet between 584 and 504 Å.

From the preceding discussion it is evident that the technique of absorption spectroscopy has no real value for the analytical determination of the inert gases, and it is fortunate that in this case emission spectroscopy provides a good means of analysis.

Molecular band spectra

The absorption spectrum of a diatomic molecule in many cases is found to be in the same spectral region as its emission spectrum. The two types of spectra need not necessarily be in the same region, however. Absorption or emission of radiation by a molecule must conform to the Franck-Condon principle, which states, in effect, that an electronic transition takes place in a time which is very short in comparison with that required for movement of the atomic nuclei. This means that transitions from any particular vibrational level on one potential curve (describing the variation of potential energy with changing internuclear distance), to some vibrational level on the second curve, are represented by vertical lines drawn from the extremities

of the vibrational level, to intersect the second curve. The vibrational levels closest to the points of intersection on this curve are then the preferred final levels for the transition. In the case of emission, the molecule is excited from the ground electronic state to a higher state after acquiring the necessary excitation energy in some processes such as collision with an energetic electron or molecule. Over a period of time, many different vibrational levels of the upper state will be populated, and there will be a corresponding large number of transitions from these levels to the various levels in the ground state allowed by the Franck-Condon principle, giving rise to a large number of bands. In the case of absorption by a gas, however, we have a very different state of affairs. Most experiments in absorption are carried out at room temperature; or at any rate at temperatures lower than about 50°. This means that the gas molecules are in the zero vibrational level of the ground electronic state, with a small number in the first vibrational level. Absorption of radiation will therefore lead to transitions between the 0 level of the ground state and the allowed levels of the upper state, with much weaker bands, if any at all, originating from the first vibrational level. This means that there will be fewer bands, in general, in an absorption spectrum of a gas than in the emission spectrum, the latter having more bands, extending to longer and shorter wavelengths than the former. Another point arising from the Franck-Condon principle, which will affect the positions of the two types of spectra, is the change in internuclear distance on going from one potential curve to the other. If there is very little difference in the internuclear distances in both electronic states, the verticals drawn from a vibrational level in one will intersect the other curve around the same place, and absorption and emission spectra will lie in approximately the same wavelength region. If there is a large change in the internuclear distance, however, this will not be so. The verticals from a vibrational level on one curve will intersect the other at a different level, leading to a difference in the positions of emission and absorption spectra.

The appearance of an absorption spectrum is further simplified in comparison with the corresponding emission spectrum, by virtue of the much simpler rotational structure in the former case. This again results from the fact that most absorption work is done at or near room temperature, where only the lower rotational levels have appreciable populations. This leads to a relatively small number of lines originating from the ground state rotational levels, whereas in the case of emission, the temperature is necessarily much higher, resulting in a large number of rotational levels being populated in the upper state, and a correspondingly greater number of lines. Consequently in practice it is easier to pick out band heads in absorption than in emission.

The absorption spectrum of a gas may be used in an exactly similar fashion to its emission spectrum, for purposes of qualitative identification. The use of absorption spectroscopy for quantitative analysis depends on two physical laws. The first, proposed by Lambert, states that when a beam of radiation passes through a homogeneous absorbing medium the intensity of the radiation is reduced by the same fractional amount in each succeeding unit length of the path. This can be stated in the form

$$-\frac{dI}{I} = kl \tag{1}$$

where I is the intensity at any point and k the fraction by which the absorbing material

reduces the intensity for unit path length; k is known as the absorption coefficient. Integration of this expression between the limits 0 and x, where x is the total path length traversed by the radiation, gives us for the ratio I_0/I_x

$$\log_{10} \frac{I_0}{I_x} = Kx \tag{2}$$

or

$$I_x = I_0 \cdot 10^{-Kx} \tag{3}$$

Here I_0 is the intensity of the incident radiation and I_x the intensity after passing through the thickness x.

The second law, first enunciated by Beer, states that the amount of absorption depends directly on the amount of absorbing species present, or on its concentration if it is in solution. For gases, the second law is incorporated in expression (3) by reducing the gas pressure to S.T.P. and then calculating the hypothetical path length, x, which would give the same absorption as that obtained under the actual experimental conditions.

The factor $\log_{10} I_0/I_x$ in expression (2) is usually known as the optical density, and is designated D.

Some workers prefer to use the absorption coefficient k, obtained from (1) using natural logarithms. Integration of (1) in this way gives us,

$$\log_e \frac{I_0}{I_x} = k \cdot x \tag{4}$$

and

$$I_x = I_0 \exp(-kx) \tag{5}$$

Obviously the two coefficients k and K are related by

$$k = 2{\cdot}303\ K \tag{6}$$

In order to obtain accurate and meaningful values of the absorption coefficient for gases which give a discrete band structure, a resolution is required which can separate individual rotational lines. This is usually the case for simple molecules, *e.g.*, diatomic, triatomic and a few more complex molecules. When the absorption consists of diffuse bands or continua, however, high resolution is not required, and as a rule Beer's law holds rigorously at relatively low pressures. This is the case for most polyatomic molecules. For very sharp bands, such as those obtained in the Schumann-Runge system of oxygen, if the resolution is not good enough to resolve the rotational structure completely, the values of k or K which are obtained will most probably show an apparent variation with pressure. A good review of absorption laws is given by Nielson, Thornton and Dale.[6]

EXPERIMENTAL METHODS OF OBTAINING SPECTRA

(*a*) *Light sources*

For work in the visible region of the spectrum, the tungsten filament lamp is still the one most commonly employed. For absorption work the source must be one of stable operating characteristics and high brightness. Various modifications of the simple filament lamp have been developed and are described in the standard texts.[7,8,9]

For the ultraviolet region down to about 2000 Å, various gas discharge tubes are available, the most commonly used being the hydrogen tube and the xenon tube. One of the most important characteristics that a good discharge tube must possess for such work is the emission of a near uniform continuum with as few atomic lines as possible. Both of the above mentioned tubes fulfil this condition fairly well.

Below 2000 Å, *i.e.*, in the vacuum ultraviolet region, a variety of sources have been tried, with varying degrees of success. Lee and Weissler[10] have employed a low pressure spark for measurement of absorption intensities between 300 Å and 1300 Å, using a photographic technique. They claim a constancy of this source of the order of 2%, but it has the disadvantage of a strong line emission superimposed on the continuum.

The most common source for this region is the hollow cathode discharge tube, modified by the inclusion of a quartz or glass capillary section in the cathode assembly, operating at about 600 V and 0·5 A d.c. The tube may be filled with hydrogen or inert gas (usually xenon) and is fitted with a window of LiF or CaF_2. More recent developments in this field are concerned with the use of electrodeless lamps, the gas being excited by a microwave discharge.[11]

(*b*) *Absorption cells*

The characteristics required of a vessel used to contain the gas to be investigated are principally

(i) good transmission through the cell windows in the desired spectral region,
(ii) sufficient path length to give appreciable absorption (this will depend on how intensely a given gas absorbs and the pressure of gas used),
(iii) ease of manipulation, *e.g.*, for cleaning purposes and degassing of cell walls,
(iv) reasonable flatness and parallelism of end windows.

The standard texts on absorption spectroscopy give details of the most commonly used types of cell for various purposes. Here it will suffice to say something on the types of window used. For work in the visible region polished glass windows are sufficient; they will transmit radiation in the region 10,000–3500 Å. Below this region polished quartz plates must be employed. The use of quartz extends the spectral range down to about 2100 Å. If it is desired to go to even shorter wavelengths, materials such as LiF or CaF_2 can be used. These materials can be used for wavelengths down to 1200 Å, but to investigate this region all air must be removed from the light path since oxygen begins to absorb strongly below 2000 Å. This necessitates the use of vacuum spectrographs with LiF or CaF_2 optics, or reflection grating instruments.

(*c*) *Measurement of absorption intensity*

The measurement of absorption intensity involves essentially the same procedure as emission intensity measurements and this has been discussed in Part I. Again photographic or photoelectric techniques can be used, present trends favouring the use of photoelectric spectrophotometers.

THE ABSORPTION SPECTRA OF GASES AND VAPOURS

Inorganic vapours and gases

The reference work of Pearse and Gaydon[12] lists the wavelengths of the major band heads of the absorption spectra of many inorganic compounds in the vapour

form. Among the absorption spectra listed are those obtained from the halide salts of silver, aluminium, barium, bismuth, calcium, copper, gallium, indium, magnesium, manganese, lead, selenium, tin, strontium, tellurium, thallium and a number of interhalogen compounds. Also listed are the spectra obtained from the oxides of lead, chlorine, selenium, tin and tellurium; the hydrides of aluminium, barium and copper; the sulphides of germanium, lead and tin; and the selenides and tellurides of silicon, tin and lead. The absorption spectra of the vapours of many elements have been examined and those listed include arsenic, bismuth, bromine, cadmium, chlorine, caesium, mercury, iodine, indium, potassium, lithium, phosphorus, lead, antimony, selenium and tellurium.

The same set of wavelength tables record data for the absorption spectra of oxygen, ozone, sulphur dioxide, nitrous oxide, nitrogen peroxide, ammonia, nitrous acid, isocyanic acid, cyanogen and carbon disulphide.

Organic vapours

The absorption spectra of organic vapours have not been so conveniently tabulated as those derived from inorganic species. Pearse and Gaydon[12] only record spectral data for acetylene, benzene, formic acid, formaldehyde, acetaldehyde, propionaldehyde, acetone, benzaldehyde, glyoxal, methyl nitrite and ethyl nitrite. The complexity of the molecular band spectra obtained from organic vapours renders the preparation of a set of tables, similar to those in existence for atomic species and inorganic molecular species, extremely difficult, but as most individual publications include photographs and tables of wavelengths, a source of references to relevant data could prove equally useful. Thus in the following sub-sections, reference is given to recent publications related to the various compounds. In order to restrict the extent of this paper, compounds which absorb in the vacuum ultraviolet have not been included.

A number of models and methods of calculation have been proposed for theoretical studies on the electronic structures of molecules and the prediction of the effect of substituents on the spectrum of a parent compound. This aspect will not be discussed in this paper but details can be found in the publication of Duncan and Matsen[4] or in recent papers such as that by Moffit[13] on the electronic spectra of cata-condensed hydrocarbons; those by Ham and Ruedenberg[14] on the spectra of aromatic hydrocarbons; that by Goodman *et al.*[15] on the spectra of substituted aromatic hydrocarbons; or those by Anno[16] on the electronic structure of the N-containing heterocyclic molecules. Much other relevant material will be found in the publication by Gillam and Stern.[2]

Benzene: The absorption spectrum of benzene in the region between 2200 Å and 2800 Å was analysed by Sponer *et al.*[17] in 1939; and a year later Radle and Beck[18] determined the wave numbers and relative intensities of five hundred of the absorption bands in the 2600 Å region. In the same year the absorption spectrum of heavy benzene found in the region of 2700 Å–3000 Å was analysed,[19] and this was followed by a study of the absorption spectrum of monodeuterobenzene, which absorbs in the same region as benzene.[20] The far ultraviolet absorption spectra and ionisation potentials of C_6H_6 and C_6D_6 were examined by Price and Wood,[21] and an attempt to give a coherent interpretation of the absorption systems of benzene vapour in this region was made by Nordheim, Sponer and Teller.[22] The work of Price and Wood

has been re-examined by Wilkinson[23] using a 21-ft grating instrument and the increased dispersion facilitated the identification of many new weak bands. The variation of the benzene spectrum with temperature was re-examined by Kistiakowsky and Solomon,[24] and from the Boltzmann distribution function two fundamental frequencies of the normal state were deduced. A detailed study of the variation in intensity of the main band of three progressions with temperature was included in the study of Radle and Beck.[18] The effect of high pressure was examined by Robertson, Babb and Matsen[25] and the benzene absorption bands were found to broaden asymetrically, and to shift to longer wavelengths on increasing the partial pressure of a foreign gas. In another study[26] the absorption spectra was examined in the presence of diluent gases over a wide range of densities, and the red spectral shifts were found to be linear functions of the density.

Halogen substituted benzenes: The absorption spectrum of monochlorobenzene found in the region 2400 Å–2700 Å has been analysed by Sponer and Wollman.[27] Detailed interpretations of the spectra of *o*- and *p*-dichlorobenzene vapours which consist of 300 bands in the region 2400 Å–2900 Å, and 400 bands in the region 2400 Å–2950 Å, respectively, are described by Anno and Matubara.[28] The absorption spectrum of 1,2.4,5-tetrachlorobenzene vapour was photographed by Matubara and Anno[29] and was found to consist of 150 bands in the region 2650 Å-3040 Å, with continuous absorption below 2500 Å.

A re-investigation of fluorobenzene by Wollman[30] showed that the spectrum was similar to that of chlorobenzene and was composed of over 280 bands in the region 2380 Å–2750 Å. Cooper[31] examined the spectrum of *p*-difluorobenzene over a wide range of temperatures and identified over 600 bands between 2350 Å and 2900 Å. The observed wavelength shifts of the O,O bands in the near ultraviolet spectra of a number of fluorinated benzenes were described by Sponer[32] who in conjunction with Rao[33] also reported data for the spectrum of 1,2,4-trifluorobenzene vapour.

Bands in the spectrum of *o*-fluorochlorobenzene were identified by Krishnamachari[34] who later reported results on the spectra of *o*-, *m*- and *p*-fluorobromobenzenes.[35] Another report on the *m*-isomer of the last compound has been made by Tintea *et al.*[36]

Alkyl substituted benzenes: An absorption spectrum composed of over 200 bands in the region 2390 Å–2760 Å was observed by Ginsberg *et al.*[37] in a study of toluene vapour. The absorption behaviour of *o*- and *m*-chlorotoluenes was investigated by Swamy.[38]

The absorption spectra of the dimethylbenzenes have been studied by Cooper and co-authors[39,40] and Singh.[41] The spectra between 2350 Å and 2850 Å were photographed and analysed. The *m*-isomer has the least number of bands and the most diffuse appearance, while the *o*-isomer consists of many very sharp bands.

In the re-examination of aniline, over 500 lines were found in the region 2500 Å–3000 Å.[42] The presence of a nitro group moves the absorption region to longer wavelengths, so that the bands of *o*- and *m*-nitroaniline were found in the regions 2700 Å–3600 Å and 2550 Å–3250 Å, respectively.[43] The absorption bands of the toluidines have been photographed and discussed.[44]

The spectrum of benzonitrile vapour was examined by Hirt and Howe[45] and found to resemble closely the spectra of other mono-substituted benzenes. The spectrum of toluonitrile vapour has been re-investigated and re-classified by Sen.[46]

Oxy-substituted benzenes: The absorption spectrum of phenol has been shown[47] to be composed of over 330 bands covering the region 2490 Å–2830 Å. The absorption region for the nitrophenols was found at longer wavelengths, and the wavelength of maximum absorption was found to decrease in the order of *o-* > *m-* > *p*-isomer.[48]

The *p*-cresol spectrum was found by Imanishi *et al.*[49] to consist of over 170 bands in the 2480 Å–2945 Å region. The thiocresols have been studied by Bapat[50,51] and bands are reported for the three isomers within the range 2590 Å–2920 Å. The exited state frequencies of these compounds were compared with those of thirteen other disubstituted benzenes.

Benzaldehyde vapour absorption has been investigated by Imanishi, who reports bands in the region 2480 Å–2970 Å,[52] and a large number of narrow bands in the region 3163 Å–3747 Å.[49] Weak vapour absorption in the regions 3060 Å–3500 Å and 3270 Å–3510 Å were also found[49] using acetophenone and benzophenone, respectively.

Dual regions of absorption bands have also been reported for the *o-* and *m*-hydroxybenzaldehydes by Achyuta and Rao.[53] The *p*-isomer exhibited bands in only one region, namely 2915 Å–2660 Å. Patel[54] has demonstrated that the effect of chloro-substitution in benzaldehyde is to shift the long wave benzenoid system to longer wavelengths, the magnitude of the shift being in the order of *o-* > *m-* > *p*-isomer.

The vapour absorption of benzoquinone has been examined by Singh, who records about 130 bands between 2254 Å and 3084 Å[55] and an even larger number of sharp bands in the region 4100 Å–5000 Å.[56] A vibrational analysis of the absorption spectrum in the region 4080 Å–5100 Å has recently been published by Anno and Sado.[57]

Heterocyclic Compounds: The absorption spectrum of pyridine in the region 2500 Å–3000 Å has been re-examined by Sponer and Stucklen, who made a vibrational analysis of the 160 bands observed.[58] Another 60 bands in the region 3000 Å–3300 Å were fitted into a vibrational scheme by Reid,[59] but these bands were later shown by Brealey[60] to be caused by a trace of impurity (pyrazine) in the pyridine used in the previous studies. A vibrational analysis of the absorption spectrum of pyrazine vapour has been proposed by Ito *et al.*[61] and another proposed assignment has been published by Hirt,[62] who included a study of chloropyrazine. The spectrum of pyridine-*N*-oxide was found to be similar in many respects to the spectrum of pyridine, except that the 250 bands are located at longer wavelengths.[63]

Absorption studies of the three isomeric picolines have been made by Sponer and Rush.[64,65] All three compounds showed a few diffuse bands in the region 2450 Å–2700 Å, and narrow, relatively sharp bands in the region between 2700 Å and 3000 Å.

The wave numbers of 112 absorption bands of pyrimidine vapour in the 2700 Å–3300 Å region have been determined by Uber.[66] The absorption spectra of the diazines have also been studied by Halverson and Hirt,[67] and similar studies were extended by Mason[68,69] to include sym-triazine, 3,5,6-trimethyl-1,2,4-triazine, *m*-tetrazine and sym-tetrazine. The spectrum of pyrrolidine vapour between 2300 Å and 2800 Å was studied over a range of temperatures by Santhamma,[70] and 61 broad and diffuse bands were measured.

Condensed ring compounds: The vapour absorption spectra of light and heavy naphthalenes found in the region 2500 Å–2900 Å have been recorded by Sponer

and Cooper,[71] and the spectroscopic behaviour of a large number of methyl derivatives of naphthalene were measured by Wolf.[72] The spectra of the derivatives were found to be very similar to that of the parent compound. The spectra reported by Deb[73] for 1-chloro- and 1-bromonaphthalene also fall within the same wavelength region.

Vibrational assignments were made by Bapat[74] for the 60 bands in the region 2500 Å–2800 Å found in the absorption spectrum of tetrahydronaphthalene.

The absorption spectra of the vapours of anthraquinone and a number of derivatives are included in the recent work of Borisevich and Gruzinskii.[75]

Miscellaneous compounds: The ultraviolet absorption spectrum of formaldehyde[76] has been re-investigated, and a complete analysis of the acetaldehyde spectrum reported.[77] Vibrational assignments have also been made for the bands observed in the spectrum of cyclopentanone,[78] and spectra have been recorded for crotonaldehyde,[79] the three isomeric methylphenetoles,[80] *m*- and *p*-methylanisoles,[81] *o*- and *p*-chlorophenetoles,[82] and tropolone.[83]

The absorption spectrum of acetone vapour has been well known for years,[84] but quite recently a study has been made of the spectra of twenty alkyl-, cyclo-alkyl- and chloro-substituted ketones.[85] This latter study was made in order to compare the influence of the positive inductive effect of the methyl with the negative inductive effect of the chloro group.

Vibrational analysis of the spectrum obtained from acetylene[86] and diacetylene[87,88] have been made, and a spectrum for dicyanoacetylene[89] has been reported for the first time. The intense absorption of 1,3-cyclohexadiene vapour in the ultraviolet region has been examined by Henri and Pickett,[90] and the behaviour of the vapours of the three isomers of phenylenediamine has been studied by Sado and Anno.[91] The ester, *n*-butyl benzoate was included in the studies of Deb[92] who examined the influence of the physical state on the ultraviolet absorption spectra of different compounds.

DISCUSSION

From the preceding review it can be seen that there is a good background of spectral data available which could be used in chemical analysis through adoption of a vapour phase absorption technique. While the spectrographs used for analysis would probably not have the same degree of dispersion as those used in the purely "spectroscopic" studies, identification of a species from its spectrum should be readily achieved. There is the disadvantage that many species absorb in the same wavelength region, and since band spectra are more complex than atomic line spectra, identification of the components of a mixture could become difficult. There is the further disadvantage that relatively high temperatures may be needed to convert some compounds into the vapour phase. On the credit side one may list the high sensitivity of the technique; the characteristic nature of molecular spectra; and the absence of "solvent" effects. In addition, unlike the emission technique previously discussed (Part I), a leak of air into the evacuated cell does not influence the spectrum and does not produce an interfering spectrum.

However, as analysis based on a gaseous phase is usually not so convenient as a method involving liquids, the practicability of vapour phase absorption technique has been examined experimentally. The results of this study will be reported in Part III of this series.

Acknowledgment—One of us (W.F.P.) wishes to thank the Queen's University of Belfast for the award of a Research Fellowship and the University of New South Wales for a grant of study leave.

Zusammenfassung—Die Molekularabsorption von Gasen und Dämpfen wird zusammenfassend behandelt in besonderem Hinblick auf Spektren organischer Molekül.

Résumé—Les auteurs passent en revue les méthodes d'absorption électronique moléculaire des gaz et des vapeurs en insistant particulièrement sur les spectres obtenus avec des molécules organiques.

REFERENCES

[1] L. N. Ferguson, *Chem. Reviews*, 1948, **43**, 394.
[2] A. E. Gillam and E. S. Stern, *Electonic Absorption Spectroscopy*. Edward Arnold Ltd., London, 1958.
[3] G. Herzberg, *Spectra of Diatomic Molecules*. Van Nostrand, N. Y., 1950.
[4] A. B. F. Duncan and F. A. Matsen, *Chemical Applications of Spectroscopy*. Ed. W. West. Interscience, N.Y., 1956. Chap. 5.
[5] J. W. Robinson, *Analyt. Chem.*, 1961, **33**, 1067.
[6] J. R. Nielson, V. Thornton and E. B. Dale, *Rev. Mod. Phys.*, 1944, **16**, 307.
[7] W. R. Brode, *Chemical Spectroscopy*. Wiley and Sons, Inc., N. Y., 1943.
[8] G. R. Harrison, R. C. Lord and J. R. Loofbourow, *Practical Spectroscopy*. Prentice Hall Inc., N. J., 1959.
[9] M. G. Mellon, Ed., *Analytical Absorption Spectroscopy*. Wiley and Sons, Inc., N.Y., 1953.
[10] P. Lee and G. L. Weissler, *J. Opt. Soc. Amer.*, 1952, **42**, 80.
[11] M. Zelikoff, P. H. Wyckoff, L. M. Aschenbrand and R. S. Loomis, *ibid.*, 1952, **42**, 818.
[12] R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra*. Chapman and Hall, Ltd., London, 1950.
[13] W. Moffitt, *J. Chem. Phys.*, 1954, **22**, 320.
[14] N. S. Ham and K. Ruedenberg, *ibid.*, 1956, **25**, 1, 13.
[15] L. Goodman, I. G. Ross and H. Skull, *ibid.*, 1957, **26**, 474.
[16] T. Anno, *ibid.*, 1958, **29**, 1161, 1170.
[17] H. Sponer, G. Nordheim, A. K. Sklar and E. Teller, *ibid.*, 1939, **7**, 207.
[18] W. F. Radle and C. A. Beck, *ibid.*, 1940, **8**, 507.
[19] H. Sponer, *ibid*, 1940, **8**, 705.
[20] C. A. Beck and H. Sponer. *ibid.*, 1942, **10**, 575.
[21] W. C. Price and R. W. Wood, *ibid.*, 1935, **3**, 439.
[22] G. Nordheim, H. Sponer and E. Teller, *ibid*, 1940., **8**, 455.
[23] P. G. Wilkinson, *ibid.*, 1956, **24**, 917.
[24] G. B. Kistiakowsky and A. K. Solomon, *ibid.*, 1937, **5**, 609.
[25] W. W. Robertson, S. E. Babb and F. A. Matsen, *ibid.*, 1957, **26**, 367.
[26] W. W. Robertson and S. E. Babb, *ibid.*, 1958, **28**, 953.
[27] H. Sponer and S. H. Wollman, *ibid.*, 1941, **9**, 816.
[28] T. Anno and I. Matubara, *ibid.*, 1955, **23**, 796.
[29] I. Matubara and T. Anno, *ibid.*, 1956, **24**, 595.
[30] S. H. Wollman, *ibid.*, 1946, **14**, 123.
[31] C. D. Cooper, *ibid.*, 1954, **22**, 503.
[32] H. Sponer, *ibid.*, 1954, **22**, 234.
[33] K. N. Rao and H. Sponer, *Canad. J. Phys.*, 1957, **35**, 332.
[34] S. L. N. G. Krishnamachari, *Indian J. Phys.*, 1955, **29**, 603.
[35] *Idem, ibid.*, 1956, **30**, 487.
[36] H. Tintea, L. Heinrich and M. Iuga, *Studia Univ. Victor Babes, Bolyai Ser.* 1, 1959, **1**, 63: *Chem. Abs*, 1959, 55:4146.
[37] N. Ginsburg, W. W. Robertson and F. A. Matsen, *J. Chem. Phys.*, 1946, **14**, 511.
[38] H. N. Swamy, *Indian J. Phys.*, 1952, **26**, 445.
[39] C. D. Cooper and M. L. N. Sastri, *J. Chem. Phys.*, 1952, **20**, 607.
[40] C. D. Cooper and H. Sponer, *ibid.*, 1952, **20**, 1248.
[41] I. S. Singh, *J. Sci. Research Banaras Hindu Univ.*, 1956-57, **7**, 171; 1957–58, **8**, 19, 32, 44.

[42] N. Ginsberg and F. A. Matsen, *J. Chem. Phys.*, 1945, **13**, 167.
[43] V. I. Danilova, *Izvest. Vysshikh. Ucheb. Zavedenii. Fiz.*, 1958, **2**, 108.
[44] U. R. G. Biswas, *Indian J. Phys.*, 1953, **27**, 603.
[45] R. C. Hirt and J. P. Howe, *J. Chem. Phys.*, 1948, **16**, 480.
[46] S. K. Sen, *Indian J. Phys.*, 1955, **29**, 561.
[47] F. A. Matsen, N. Ginsburg and W. W. Robertson, *J. Chem. Phys.*, 1945, **13**, 309.
[48] V. I. Danilova, *Izvest. Vysshikh. Ucheb. Zavedenii. Fiz.*, 1959, **1**, 77.
[49] S. Imanishi, M. Ito, K. Semba and T. Anno, *J. Chem. Phys.*, 1952, **20**, 532.
[50] R. N. Bapat, *Proc. Indian Acad. Sci.*, 1959, **50A**, 183.
[51] *Idem, ibid.*, 1959, **49A**, 203.
[52] S. Imanishi, *J. Chem. Phys.*, 1951, **19**, 389.
[53] I. Achyuta and V. R. Rao, *Indian J. Phys.*, 1960, **34**, 196.
[54] J. C. Patel, *J. Sci. Ind. Research (India)*, 1959, **18B**, 265.
[55] R. S. Singh, *J. Sci. Research Banaras Hindu Univ.*, 1957–58, **8**, 261.
[56] *Idem, Indian J. Phys.*, 1959, **33**, 376.
[57] T. Anno and A. Sado, *J. Chem. Phys.*, 1960, **32**, 1602.
[58] H. Sponer and H. Stucklen, *ibid.*, 1946, **14**, 101.
[59] C. Reid, *ibid.*, 1950, **18**, 1673.
[60] G. Brealey, *ibid.*, 1956, **24**, 571.
[61] M. Ito, R. Shimada, T. Kuraishi and W. Mizushima, *ibid.*, 1957, **26**, 1508.
[62] R. C. Hirt, *Spectrochim. Acta*, 1958, **12**, 114.
[63] M. Ito and W. Mizushima, *J. Chem. Phys.*, 1956, **24**, 495.
[64] H. Sponer and J. H. Rush, *ibid.*, 1949, **17**, 587.
[65] J. H. Rush and H. Sponer, *ibid.*, 1952, **20**, 1847.
[66] F. M. Uber, *ibid.*, 1941, **9**, 777.
[67] F. Halverson and R. C. Hirt, *ibid.*, 1949, **17**, 1165.
[68] S. F. Mason, *J. Chem. Soc.*, 1959, 1240.
[69] *Idem, ibid.*, 1959, 1263.
[70] V. Santhamma, *Proc. Nat. Inst. Sci. India, Pt. A*, 1959, **25**, 77.
[71] H. Sponer and C. D. Cooper, *J. Chem. Phys.*, 1955, **23**, 646.
[72] H. C. Wolf, *Z. Naturforsch*, 1958, **10a**, 270.
[73] A. R. Deb, *Indian J. Phys.*, 1954, **28**, 21.
[74] R. N. Bapat, *Proc. Indian Acad. Sci.*, 1958, **48A**, 119.
[75] N. A. Borisevich and V. V. Gruzinskii, *Izvest. Akad. Nauk S.S.S.R. Ser. Fiz.*, 1960, **24**, 545.
[76] A. D. Cohen and C. Reid, *J. Chem. Phys.*, 1956, **24**, 85.
[77] V. R. Rao and I. A. Rao, *Indian J. Phys.*, 1954, **28**, 491.
[78] I. A. Rao, R. V. R. A. Rao and V. R. Rao, *J. Sci. Ind. Research (India)*, 1957, **16B**, 388.
[79] I. A. Rao and V. R. Rao, *ibid.*, 1960, **19B**, 121.
[80] K. V. K. Rao and V. R. Rao, *Indian J. Phys.*, 1960, **34**, 289.
[81] *Idem, ibid.*, 1960, **34**, 200.
[82] *Idem, J. Sci. Ind. Research (India)*, 1960, **19B**, 445.
[83] S. Imanishi and M. Ito, *J. Chem. Phys.*, 1956, **24**, 1272.
[84] A. B. F. Duncan and W. W. Manning, *ibid.*, 1934, **2**, 717.
[85] W. R. Mountcastle, D. F. Smith and E. L. Grove, *J. Phys. Chem.*, 1960, **64**, 1342.
[86] K. K. Innes, *J. Chem. Phys.*, 1954, **22**, 863.
[87] S. Woo and T. C. Chu, *ibid.*, 1935, **3**, 541.
[88] *Idem, ibid.*, 1937, **5**, 786.
[89] F. A. Miller and R. B. Hannan, *Spectrochim. Acta*, 1958, **12**, 321.
[90] V. Henri and L. W. Pickett, *J. Chem. Phys.*, 1939, **7**, 439.
[91] A. Sado and T. Anno, *ibid.*, 1955, **23**, 1740.
[92] A. R. Deb, *Indian J. Phys.*, 1954, **28**, 21.

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ANALYSIS OF GASES AND VAPOURS BY SPECTROSCOPIC TECHNIQUES—III*

APPLICATIONS OF ELECTRONIC ABSORPTION SPECTRA

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Summary—Absorption of ultraviolet radiations by the vapours of organic solvents is proposed as an alternative method of identifying the composition of small volumes of volatile liquids. The limitations of the method are discussed.

IN chemical analysis, absorption spectroscopy has become a major tool but the established techniques almost invariably involve the use of the liquid phase. Absorption by vapours does not appear to have been used in analysis. Accordingly, the possibilities of this technique were examined and were discussed in Part II of this series. Experiments on some organic vapours have now been carried out to test the usefulness of this technique and the results are reported in this paper.

EXPERIMENTAL

Apparatus and reagents

Continuous radiation from a hydrogen lamp was passed through low pressures of organic vapour contained in an absorption cell 15 cm long, 2 cm in diameter and fitted with quartz windows. A small sample container was attached to the cell by means of a ground-glass joint, and the cell was evacuated through a side-arm tap.

Small volumes of liquid (0·01 to 0·20 ml) of Analytical Grade purity were measured into the detachable sample container by means of an Agla Microsyringe and were frozen by immersion of the side-arm in a liquid nitrogen trap. The cell was then evacuated by means of an oil diffusion pump. The cell and side-arm were finally immersed in a water bath fitted with windows, and the vapour pressure in the sealed cell was adjusted by varying the temperature of the water bath.

Measurement of absorption spectra

The absorption spectrum of the vapour was photographed using a Hilger Medium Quartz Spectrograph. The source of continuous radiation used was the hydrogen discharge lamp from a Hilger Uvispek Spectrophotometer and photographs were taken on Ilford N30 plates using a slit width of 0·03 mm. An exposure time of 5 min was found to be satisfactory. The organic vapours examined included benzene, toluene, *o*-, *m*- and *p*-xylenes, benzaldehyde, aniline, ethylbenzene, pyridine and nitrobenzene.

Measurement of absorbance of benzene at 253 mμ

The absorbance of benzene vapour evaporated from benzene-hexane mixtures was measured by removing the lamp housing cover from the Uvispek Spectrophotometer, placing the absorption cell between the entrance slit and focussing the reflecting mirror on the hydrogen lamp. The check (or 100% transmission) adjustment was made using an empty cell in the light path. Known volumes of benzene-hexane mixtures were frozen in the side tube and later allowed to evaporate into the evacuated cell. The absorbance of radiation of wavelength 253 mμ by the vapour was then measured as in normal absorption studies.

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RESULTS

Absorption spectra

From the varied volumes of sample taken, the temperature of the bath and the behaviour of binary mixtures, a list of detectable limits of concentration was compiled and these are recorded in Table I.

Table 1.—Limits of detection of organic solvents

Solvent	Min. vapour pressure to give spectrum, *mm of Hg**	Min. vol. of solvent giving min. vap. press. on evaporation, (50-ml cell) *μl.*	Lowest detectable % in binary mixtures at different temperatures		
			20°	40°	60°
Benzene	0·5	0·15	1	0·3	0·2
Benzaldehyde	0·5	0·15	100	25	6
p-Xylene	0·5	0·15	10	3	2
Aniline	0·5	0·15	50	25	10
Pyridine	1	0·3	10	3	1
Toluene	1	0·3	5	2	1
Nitrobenzene†	2	0·6	—	—	80
o-Xylene	3	0·9	75	20	10
m-Xylene	3	0·9	60	20	10
Ethylbenzene	6	1·8	90	20	10

* Above a pressure of 20 mm of Hg many bands tend to broaden into a continuum, hence it is desirable to adjust the temperature to give a vapour pressure of 2–20 mm for the desired species.
† Yields a continuum only.

The photographed spectra were also used to predict the possibility of identifying one component in the presence of a second vapour and the results are recorded in Table II.

Table II.—Identifiable components of binary mixtures of aromatic solvents
(Visual comparison of spectra)

Identifiable component	Diluent solvent*
Benzene	*o*-, *m*- or *p*-Xylene, ethylbenzene, benzaldehyde, aniline, nitrobenzene
Toluene	Benzaldehyde, aniline, nitrobenzene
Pyridine	Benzene, toluene, xylenes, aniline ethylbenzene, nitrobenzene
o-, *m*- or *p*-Xylene	Benzene, aniline, nitrobenzene
Benzaldehyde	Benzene, toluene, xylenes, ethylbenzene
Aniline	Benzene, toluene, xylenes, ethylbenzene pyridine, nitrobenzene
Ethylbenzene	Benzene, benzaldehyde, aniline, nitrobenzene

* A third solvent may also be present if it does not absorb in this region of the ultraviolet (*e.g.* aliphatics like hexane) or if insufficient vapour is present to give a spectrum (nitrobenzene below 50°.)

Absorbance of benzene

Using the 15-cm cell (volume ~ 50 ml) and 0·20-ml samples, the optical density

readings were found to increase by approximately 0·1 unit for every 1% increase in benzene content in the mixture. The response varied greatly with the size of sample taken. This is to be expected, since the saturation of the cell with vapour causes a variation in the composition of the liquid phase in equilibrium with the vapour. The smaller the sample, the more marked is the variation in composition as the benzene evaporates; and accordingly the benzene vapour pressure at equilibrium cannot be calculated simply in terms of the composition of the mixture initially admitted to the cell. Correlation of the results using different sample volumes was achieved by calculating the probable value of the equilibrium pressure in each case and plotting optical density *versus* partial vapour pressure. As would be expected from theory, the relationship between absorbance and pressure was linear in the low pressure range examined (< 5 mm of Hg). The precision of the measurements, however, was poor. This can be attributed, *inter alia*, to variations in vapour pressure with temperature, errors in measuring small volumes and losses during introduction of the sample to the cell.

DISCUSSION

It can be observed from Table I that a detectable spectrum can be obtained using vapour absorption by evaporating less than 1 microlitre of solvent. Thus the technique is suitable for identifying very small volumes of pure organic solvent, but in order to achieve a suitable vapour pressure in the absorption cell, the sample and cell may have to be heated.

Since the absorption bands tend to broaden on increasing the vapour pressure and on heating the vapour, the optimum pressures observed in this study were found within the range of from 2 to 20 mm of Hg, and temperatures above 80° were not used.

In binary mixtures, it is still desirable to maintain the partial pressure of the desired component within this pressure range. The vapour pressure of a component in the mixture will be the vapour pressure of the pure component at the ambient temperature, multiplied by the molar fractional volume of the component in the liquid phase at equilibrium. In Table I, an indication is given of the influence of this molar fraction term, for in the final column values are quoted for the limit of detection (in %) of a solvent at different temperatures. It can be seen that at a given temperature (*e.g.*, 20°) the vapour pressure of some pure solvents is so low that any dilution reduces its partial pressure to a value below that detectable by the technique used. In other cases, the vapour pressure of pure solvent is sufficiently high to permit marked dilution of the liquid phase before the lower vapour pressure limit for an absorption spectrum is reached.

A second factor has to be considered if small volumes of sample or very dilute solvent mixtures are used. In these cases it is possible for all of a particular component to evaporate into the cell and still not reach the partial pressure calculated in terms of the molar fraction present in the original liquid. Under these conditions the size of sample should be increased.

The identification of a species in a mixture is complicated by the following facts: (*a*) the spectra of many benzenoid compounds overlap; (*b*) the bands of many species broaden readily into continua; and (*c*) chemical interaction between components is possible. In Table II identifications that have been achieved are recorded.

In making these identifications, the components of a mixed spectrum were identified simply by comparison with the spectra obtained with the pure substances. These standard spectra were sufficiently characteristic to permit such an approach. The identification of a species in a multicomponent system is feasible, but all other components must preferably absorb in a different region of the wavelength scale. Table II is not intended to be exhaustive, and could be extended by including many of the compounds recorded in the review which forms Part II of this series.

The quantitative studies indicate that analysis based on the vapour phase is possible but precision would need to be improved by stricter temperature control, and greater efforts would have to be made to avoid losses of vapour during sample introduction, if results of reasonable reliability are to be achieved. However, quantitative analysis based on vapour absorption does not offer any practical advantage unless the volume of liquid sample present is too small for use in a liquid micro cell or unless the liquid is extremely volatile.

The advantages that could be claimed for this vapour absorption technique are (1) that it is possible to identify the nature of a very small volume of an organic solvent (providing that it absorbs in the ultraviolet or visible range), and (2) that the time required to obtain a photographic spectrum can be much less than the time required to plot an absorption spectrum using a non-recording spectrophotometer. The technique could also prove useful for the identification of small amounts of volatile aromatic compounds present in aliphatic solvents.

However, even these advantages cannot compete in most cases with the facility of analysis now offered by the use of gas chromatography or recording spectrophotometers.

CONCLUSIONS

Vapour phase absorption spectroscopy can be proposed as an alternative method of identification and analysis of small volumes of organic solvents and within a limited range of applications may prove quite useful.

As indicated in Part II of this series, there is a good background of spectral data available, which could be utilised in development of this technique.

Acknowledgment—One of us (W.F.P.) wishes to thank the Queen's University of Belfast for the award of a Research Fellowship and the University of New South Wales for a grant of study leave.

Zusammenfassung—Die UV-Absorption von Dämpfen organischer Solventien wird als eine Methode zur Identifizierung kleiner Volume flüchtiger Substanzen empfohlen. Anwendungsmöglichkeiten der Methode werden diskutiert.

Résumé—Les auteurs proposent l'absorption des radiations ultraviolettes par les vapeurs de solvents organiques comme méthode d'identification de la composition de faibles volumes de liquides volatiles. Les limites de cette méthode sont discutées.

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SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH DIDODECYLDITHIO-OXAMIDE

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Summary—Didodecyldithio-oxamide reacts with palladium in strong hydrochloric acid solutions to form a yellow water-insoluble complex which can be extracted into chloroform. Optimum conditions for the use of the reagent have been studied. Tolerance limits for other platinum group elements and selected base metals have been determined. The procedure has been successfully applied to the determination of palladium in the presence of high concentrations of diverse ions. The sensitivity of the reaction is 0·005 $\mu g/cm^2$.

INTRODUCTION

IN recent investigations of the colour reactions of platinum and palladium with a number of symmetrically and unsymmetrically substituted dithio-oxamides,[1] didodecyldithio-oxamide was selected for further study as a reagent for palladium. Indications were that large quantities of platinum relative to palladium could be tolerated. Subsequent investigation of this reagent has shown that in addition to its high tolerance for platinum, much rhodium and ruthenium may be present, as well as high concentrations of base metals commonly associated with palladium.

There is no shortage of sensitive colour reactions for palladium. Many reactions, too numerous to mention, have been reported which exhibit greater or less selectivity. Excellent review articles[2,3] are available which discuss a variety of these methods. Reagents containing the nitrosophenylamino group, and certain dioximes, have probably found the most widespread use as palladium reagents, the latter type being superior in many respects. With the dioximes, such as α-furildioxime, palladium may be determined in the presence of relatively large concentrations of the other platinum metals. The reaction is carried out in mineral acid medium; close control of pH is not necessary and the palladium complex is readily extractable.

Conditions for colour development in the case of reagents such as *p*-nitrosodimethylaniline and *p*-nitrosodiphenylamine have to be closely controlled. These reagents are, however, among the most sensitive known for palladium.

The present paper describes a colour reaction which is both highly sensitive and not subject to close control of conditions of colour development. Unusually high concentrations of platinum, rhodium, ruthenium, cobalt, nickel, and chromium may be present. At the same time, quantities of iridium, osmium, gold, iron and copper of the order of 1 milligram may be tolerated. The complex is formed in solutions which are approximately 6.8*M* or more in hydrochloric acid. The water-insoluble complex is extracted with chloroform.

Didodecyldithio-oxamide has the following structure:

$$CH_3—(CH_2)_{11}—NH—\underset{\underset{S}{\|}}{C}—\underset{\underset{S}{\|}}{C}—NH—(CH_2)_{11}—CH_3$$

This compound has been reported to react with cobalt, nickel and copper in alkaline solution.[4] The complexes formed are water-insoluble and are not extractable by common water-immiscible solvents. With palladium, a bright yellow, water-insoluble complex is formed in the presence of high concentrations of hydrochloric acid, and this may be extracted with chloroform, carbon tetrachloride and most common organic solvents.

EXPERIMENTAL

Apparatus

Spectrophotometers: Beckman spectrophotometers, Model DK-2A and Model DU, with matched 1-cm silica cells, were used for all absorbance measurements.

Separatory funnels: Globe separatory funnels of 125-ml volume were used. The stems were shortened to approximately 1 cm.

Reagents

Standard palladium solution: A standard palladium solution was prepared by dissolving 1 g of palladium^{II} chloride in 500 ml of distilled water containing sufficient hydrochloric acid to give a final solution which was 1*M* with respect to the acid. This solution was standardised by the dimethylglyoxime gravimetric method. The solution contained 1·15 mg of palladium per ml.

Reagent solutions: The reagent is insoluble in water, only sparingly soluble in ethyl alcohol, but readily soluble in acetone. Three solutions of didodecyldithio-oxamide were prepared which contained 0·5 mg per ml., 2·0 mg per ml, and 5·0 mg per ml, respectively, of the reagent in acetone.

Solutions of diverse ions: Stock solutions containing approximately 1 mg per ml of the ions were prepared from analytical-grade chlorides or nitrates of the metals, except for osmium which was prepared from potassium osmate.

Description of the palladium complex

Colour: Didodecyldithio-oxamide forms a yellow, water-insoluble complex with palladium in the presence of high concentrations of hydrochloric acid. The complex can be extracted into chloroform. Fig. 1 shows absorbance curves for the palladium complex (4·6 ppm) and the reagent ($4{\cdot}4 \times 10^{-3}M$) The absorbance of the complex was measured against a reagent blank; that of the reagent against a distilled water blank. The palladium complex has an absorbance maximum at 450 mμ.

Effect of hydrochloric acid concentration: The concentration of hydrochloric acid was varied from 0·77*M* to 9·2*M* by the addition of 1, 3, 6, 9, and 12*M* hydrochloric acid to determine the optimum

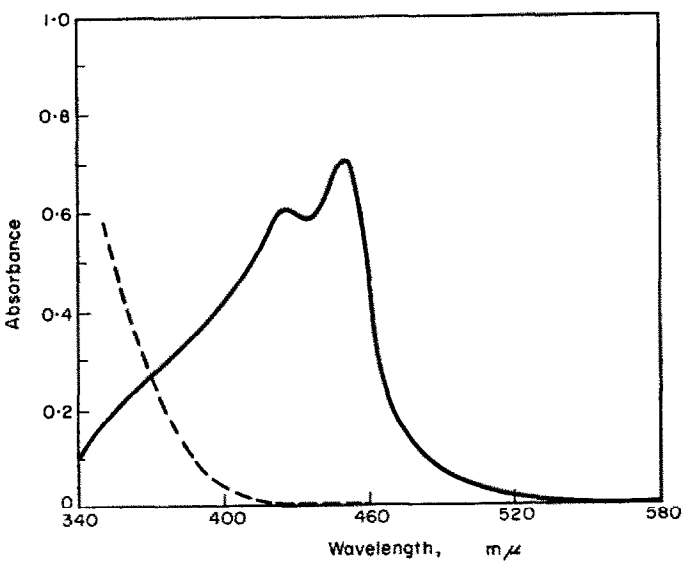


FIG 1.—Absorbance curves for the palladium complex (4·6 ppm) and reagent ($4{\cdot}4 \times 10^{-3}M$).
– – – – – Reagent
———— Palladium.

concentration for complex formation. Each sample contained 4·6 ppm of palladium, 10 ml of the acid, and 2 ml of the 2 mg/ml reagent solution. The samples were extracted with two 5-ml portions of chloroform, the extracts were diluted to 25 ml with chloroform, and the absorbances were measured. The results of this experiment are shown in Fig. 2. The absorbance of the complex begins to level off above a hydrochloric acid concentration in the aqueous phase of 6·8*M*. The gain in sensitivity above

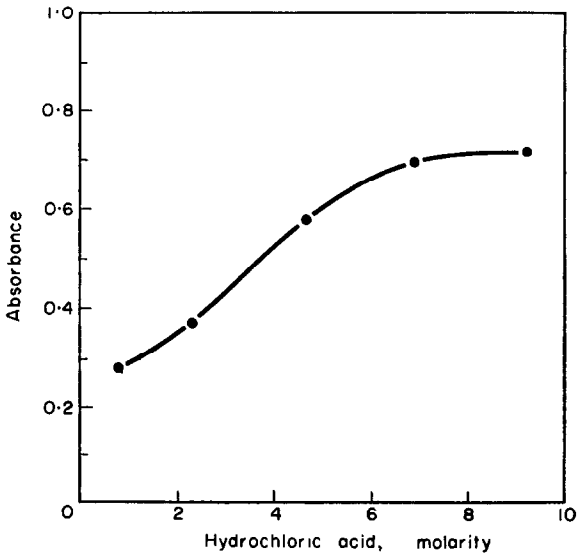


FIG. 2.—Effect of the molarity of hydrochloric acid on the palladium complex.

this acid concentration is so slight that reproducible results are obtained without rigorous control of the acid concentration. In our work, 10 ml of concentrated hydrochloric acid (12*M*) was used in an approximate volume of 16 ml. This corresponds to an acid concentration in the aqueous phase of about 7·5*M*.

Rate of colour formation: Although the yellow colour of the palladium complex formed immediately upon the addition of the reagent solution, maximum absorbance was not reached until the colour was allowed to develop for 15 min. To determine the optimum time for colour formation, samples were prepared containing 4·6 ppm of palladium, 10 ml of concentrated hydrochloric acid, and 2 ml of the 2 mg/ml reagent solution. The samples were allowed to develop for varying lengths of time after which they were extracted with two 5-ml portions of chloroform and diluted to 25 ml with chloroform. The absorbances of the samples were measured at 450 mμ against a reagent blank. Table I contains the results of this experiment.

Stability of colour: In order to check the stability of the extracted complex on standing, the absorbance of a sample was measured at intervals of 0·5 hr, 3 hr, 24 hr, and 48 hr. There was no change in absorbance over this period of time. Longer periods were not investigated.

Extraction of the complex: The number of chloroform extractions necessary for complete removal of the complex was determined by the following experiment: 4 samples were prepared which contained 3·68 ppm of palladium, 10 ml of concentrated hydrochloric acid, and 2 ml of the 2 mg/ml reagent solution. Fifteen min were allowed for maximum colour formation. These samples were

TABLE I.—RATE OF COLOUR FORMATION

Time, *min*	Absorbance at 450 mμ
immediately	0·828
5	0·830
10	0·835
15	0·842
30	0·842
60	0·843

extracted with one, two, three and four 5-ml portions of chloroform, respectively. The results, as shown in Table II, indicate that the complex is completely extracted by the use of two 5-ml portions of chloroform.

TABLE II.—EXTRACTION OF COMPLEX

Number of 5-ml chloroform extractions	Absorbance at 450 mμ
1	0·632
2	0·675
3	0·678
4	0·678

Effect of reagent concentration: Maximum colour formation is attained as long as there is a four-fold or greater excess of the reagent over palladium. Reagent concentrations considerably larger than the theoretical are used in actual practice, for reasons which will be discussed later.

Adherence to Beer's law: The palladium complex obeys Beer's law over the concentration range investigated, 0·46 to 4·6 ppm.

Optimum concentration range: According to Sandell[5] the most favourable range for making absorbance measurements is from 0·2 to 0·7 absorbance unit. This corresponds to concentrations of palladium ranging from 1·2 to 3·9 ppm.

Sensitivity: The sensitivity of the colour reaction, based upon the Sandell notation,[6] is 0·005 μg per cm^2.

Effect of diverse ions: In order to determine the effect of selected ions on the colour reaction, solutions containing approximately 1 mg per ml of the foreign ions were prepared and added individually to solutions containing 115 μg of palladium, 10 ml of concentrated hydrochloric acid, and 5 ml of a 5 mg/ml reagent solution. The samples were extracted with two 5-ml portions of chloroform and diluted to 25 ml with chloroform, and the absorbances were determined at 450 mμ. An interference was arbitrarily chosen as that concentration of the ion which produced an error of 3% or more in the amount of palladium found. The results of this experiment are shown in Table III. In the presence of approximately 1 ml of 1*M* sodium sulphite, slightly larger concentrations of gold, osmium, and iron could be tolerated. However, if platinum is present, sodium sulphite cannot be used, since the platinum will be reduced to the reactive bivalent state which will react with the reagent.

TABLE III.—EFFECT OF DIVERSE IONS (115 μg of palladium)

Ion added	Amount added, *mg*	Palladium found, *μg*	% error
Pt^{IV}	18·6	120	4·3
Ir^{IV}	1·3	119	3·5
Rh^{III}	14·3	116	0·9
Ru^{III}	14·7	116	0·9
Os^{VI}	0·2	121	5·2
Os^{VI}[a]	0·3	119	3·5
Co^{II}	10·0	112	2·6
Ni^{II}	10·0	115	0
Cu^{II}	1·0	119	3·5
Cr^{III}	6·0	113	1·7
Fe^{III}	1·1	118	2·6
Fe^{III}[a]	2·5	119	3·5
Au^{III}	0·6	118	2·6
Au^{III}[a]	3·0	118	2·6
Nitrate	5·0	116	0·9
Sulphate	5·0	116	0·9

[a] These samples contained approximately 1 ml of 1*M* sodium sulphite.

Fourteen mg of rhodium or ruthenium produce practically no interference with the palladium complex. This indicates that still higher concentrations of these ions can be tolerated with the quantity of reagent solution used. The low palladium values for large amounts of cobalt, nickel and chromium indicate that these ions consume so much of the reagent that there is an insufficient quantity for the palladium. By increasing the quantity of reagent solution, larger quantities of these ions probably can be tolerated. Copper, on the other hand, appears to react with the reagent to produce a complex which is extracted to a certain extent, since this element begins to interfere when there is approximately 1 mg present. The outstanding feature of this method is without a doubt the large concentration of platinum which can be tolerated.

Recommended procedure and analysis of synthetic samples

Recommended procedure: Introduce an aliquot of the sample (5 ml or less) which contains 30 to 100 μg of palladium into a 125-ml short-stem separatory funnel. Add 10 ml of concentrated hydrochloric acid and 5 ml of the 5 mg/ml reagent solution. Allow to stand for 15 min and extract with two 5-ml portions of chloroform which has been equilibrated with 6*M* hydrochloric acid. The use of the equilibrated chloroform gives slightly better results, possibly because it reduces the passage of highly coloured chloro-complexes into the non-aqueous phase. Dilute the sample to 25 ml with chloroform and measure the absorbance of the sample at 450 mμ. Determine the palladium content from a calibration curve. If sodium sulphite is added to increase the tolerance for osmium, iron and gold, it should be added before the addition of the acid. As was mentioned earlier, if platinum is present, sodium sulphite cannot be used.

Analysis of synthetic samples: The procedure outlined above was applied to a series of synthetic samples containing varying quantities of the other platinum metals and selected base metals along with palladium. Since the volumes of these solutions were relatively large (approximately 25 ml), the samples were concentrated by heating on a hot plate to a volume of about 1 ml. The samples were washed into separatory funnels with two 2-ml portions of distilled water and analysed by the recommended procedure. The results are given in Table IV.

TABLE IV.—ANALYSIS OF SYNTHETIC SAMPLES

Sample	Palladium added, μg	Palladium found, μg	Ions added, *mg*
1	115	124	Pt^{IV}, 13·8 Ru^{III}, 4·9 Rh^{III}, 5·3 Ir^{IV}, 1·8 Os^{VI}, 0·3
2	115	122	Same as 1
3	115	114	Pt^{IV}, 13·8 Ru^{III}, 4·9 Rh^{III}, 5·3
4	57·5	59·2	Same as 3
5	115	118	Pt^{IV}, 13·8 Ru^{III}, 4·9 Rh^{III}, 5·3 Ni^{II}, 4·0 Co^{II}, 5·0 Fe^{III}, 1·0 Cu^{II}, 1·0
6	115	110	Pt^{IV}, 20·7 Ru^{III}, 4·9 Rh^{III}, 5·3 Ir^{IV}, 0·9
7	57·5	62·3	Same as 6

CONCLUSIONS

Didodecyldithio-oxamide has been shown to react rapidly in strong hydrochloric acid solutions with palladium to give a water-insoluble complex which may be extracted with chloroform. Conditions for the development of colour need not be rigorously controlled. The reaction has a sensitivity which compares favourably with other palladium reagents. The high tolerance for other platinum metals and certain base metals should result in the proposed procedure's extensive use as a method for palladium.

Acknowledgement—Financial assistance from the National Science Foundation in the form of a research grant to W. D. J. is gratefully acknowledged.

Zusammenfassung—Didodecylidithiooxamid reagiert mit Palladium in stark salzsaurem Medium zu einem gelben, wasserunlöslichen Komplex, der in Chloroform ausgezogen werden kann. Die optimalen Bedingungen wurden erarbeitet. Die Störungsgrenzen für andere Platin- und einige weitere Metalle wurden ermittelt. Die Methode wurde auf die Bestimmung von Palladium in Gegenwart hoher Konzentrationen verschiedener, anderer Ionen angewendet. Die Empfindlichkeit der Reaktion ist 0·005 μg/cm^2.

Résumé—Le didodecyldithio-oxamide réagit avec le palladium en milieu acide chlorhydrique concentré pour former un complexe jaune, insoluble dans l'eau, qui peut être extrait par le chloroforme. Les meilleures conditions d'utilisation du réactif ont été étudiées. Les limites de tolérance pour les autres éléments du groupe du platine et pour des métaux choisis ont été déterminées. La méthode a été appliquée avec succès au dosage du palladium en présence de grandes concentrations de divers ions. La sensibilité de la réaction est 0,005 μg/cm^2.

REFERENCES

[1] W. D. Jacobs and J. T. Pyle, unpublished results.
[2] F. E. Beamish and W. A. E. McBryde, *Analyt. Chim. Acta*, 1953, **9**, 349.
[3] *Idem, ibid.*, 1958, **18**, 551.
[4] W. D. Jacobs and J. H. Yoe, *Proceedings of the Symposium on the Chemistry of Co-ordination Compounds*, Agra, 1959, Part III, pp. 265–273.
[5] E. B. Sandell, *Colorimetric Determination of Traces of Metals*. Interscience Publishers, New York, 3rd Ed. 1959, p. 97.
[6] *Idem, ibid.*, p. 83.

Talanta, 1962, Vol. 9, pp. 249 to 263. Pergamon Press Ltd. Printed in Northern Ireland

PHOTOMETRIC TITRATIONS—VI*

THE DETERMINATION OF SUBMICROGRAM QUANTITIES OF CALCIUM AND MAGNESIUM

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Summary—Three different types of end-point detection in photometric titrations are defined, and their relation to the selectivity problem is discussed. Some of the principles are applied to the determination of calcium and magnesium in quantities down to a few tenths or hundredths of a microgram. Excess dye (Calmagite) is added to the solution containing calcium and magnesium buffered to pH 10, so that both metals are complexed. Then the titration is performed with EDTA. A titration curve is obtained with two end-points, thus allowing the evaluation of each metal present. Changes effected in a photometric titrator previously described are discussed, as well as their relation to increased sensitivity and precision.

END-POINT detection in photometric titrations involves both equilibrium and optical (absorbance) properties of the system. When the discussion is restricted to titrations based on the formation of a 1:1 complex, the following mechanisms of indication can be differentiated:

(1) *Self-indication:* A system is said to exhibit self-indication when a metal ion initially present in a complex (B-complex) is progressively transferred into the titration complex (T-complex) of differing absorbance upon addition of titrant. The conditions which must be satisfied in order that a titration might be possible are: the stability constant of the T-complex must be sufficiently higher than that of the B-complex to allow the transfer to the metal ion to be essentially complete; the stability of the T-complex and also of the B-complex, when the latter is an optically significant variable, must be high enough to ensure that neither is appreciably dissociated; the absorptivities of all species involved must be such that the slopes of the two straight branches of the titration curve are sufficiently different to permit a well-defined intersection to be obtained upon extrapolation.

Example 1: An example of a self-indicating system is the EDTA titration of copper at pH 5.[1] Copper is initially present as the weakly absorbing aquo-complex (B-complex) and during the titration the more stable and more absorbing EDTA complex (T-complex) is formed. Both complex formers, water and EDTA, are colourless and hence do not need to be taken into account optically. The type of curve obtained is shown as curve I in Fig. 1.

Example 2: Copper can also be titrated with EDTA at pH 10 in ammoniacal solution. The highly coloured tetrammine complex is the B-complex, and during the titration the less absorbing EDTA complex (T-complex) is formed. Again, the B- and T-complex formers do not need to be taken into account optically. The concentration of the B-complex former (ammonia), however, affects both the degree of dissociation of the B-complex and the ratio of the stability constants of the two complexes (effect of the β-factor). A curve of type II in Fig. 1 results from such a titration.

* Part IV, *Talanta*, 1962, **9**, 76: Part V, *Talanta*, 1961, **8**, 885.

(2) *Step-indication:* The term step-indication will be used to describe a system in which a complex forming indicator is employed to obtain a step-like change in absorbance when the end-point is approached. The following conditions must be satisfied: the stabilities of the T-complex and I-complex (indicator-complex) must be sufficient to prevent an unduly high degree of dissociation; the magnitude of the stability constants, for obvious reasons, must be in the order $K_B \ll K_I \ll K_T$, where

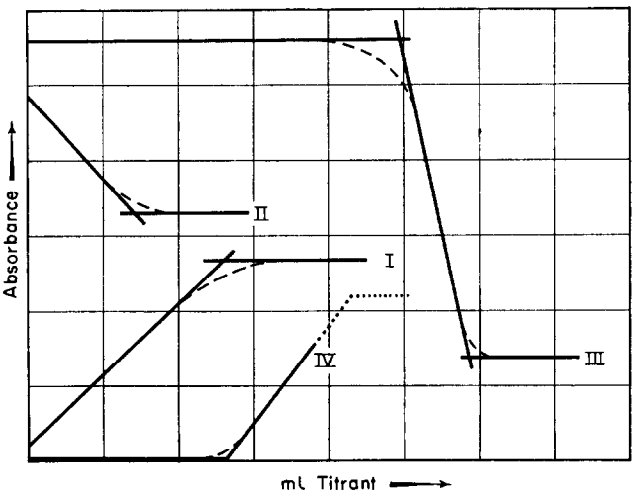


FIG. 1.—Titration curves obtained with various types of indication.

the subscripts refer to the appropriate complexes; the absorptivities of all species involved must be such that a well-defined intersection is obtained upon extrapolation.

Example 3: Step indication is exemplified by the EDTA titration of copper at pH 4 using PAN as indicator.[2] The type of curve obtained is represented by curve III in Fig. 1. The first horizontal portion of the titration curve results when copper is transferred from the aquo-complex (B-complex) to the EDTA complex (T-complex), neither of which absorbs at the wavelength selected. In contrast with the self-indicating system, this portion of the curve is not used for the extrapolation and hence need not be plotted in practice. The second portion, where an abrupt change in absorbance occurs, is obtained when copper is transferred from the I-complex to the T-complex. The third part results upon the addition of colourless titrant after the end-point has been reached.

It is important to note that a step-indicated system shows two intersection points, the second generally corresponding to the amount of metal determined. The difference between the two points is equivalent to the amount of indicator present.

(3) *Slope-indication:* The term slope-indication will be used to describe end-point location *via* a self-indicating system, the metal of which is titrated after the metal to be determined. Again, the T-complexes must be stronger than the corresponding B-complexes. The T-complexes and any optically significant B-complex must be strong enough to prevent any appreciable dissociation. In addition the condition

$$(K_T/K_B)_s \ll (K_T/K_B)_d$$

must be satisfied, *i.e.*, the ratio of the stability constants of the T- and B-complexes of

the self-indicating system (subscript "s") must be less than the ratio of the stability constants of the corresponding complexes of the metal to be determined (subscript "d"). These conditions ensure that the metal to be determined is complexed before the metal in the self-indicating system. The absorptivities of all species involved must be such that the slopes of the titration curve before and after the end-point differ sufficiently to permit a precise location of the end-point by extrapolation.

Example 4: One of the first systems involving slope-indication was studied by Underwood[3] when he titrated bismuth with EDTA using copper as the so-called "photometric indicator".* The type of titration curve obtained is shown as curve IV in Fig. 1. The first horizontal part of the curve corresponds to the transfer of bismuth from the aquo- to the EDTA complex, neither of which absorbs. When all the bismuth is titrated, copper is complexed by the EDTA and the absorbance increases through the formation of the strongly absorbing Cu-EDTA complex. The titration may be stopped at any point of the inclined part of the curve when the number of points recorded suffices for the extrapolation of the straight line.

It may be mentioned that in the case where both bismuth and copper are to be determined, the titration may proceed along the dotted line to a second intersection indicating the end-point of the copper titration.[3]

In the titration of a metal which is present alone in a solution, the several methods of end-point detection, self-, step- and slope-indication, are equally satisfactory. However, when a metal is to be determined in the presence of others, the method of end-point detection has a very close bearing on the selectivity problem. The following examples will serve to elucidate the situation. Let it be required to determine copper in the presence of aluminium in acetic acid medium. The EDTA complex of copper is more stable than that of aluminium, and copper reacts with the indicator, PAN, whereas aluminium does not. It would seem at first glance that a selective titration of copper under these conditions is possible. However, only the sum of the two metals can be obtained,[4] as will be apparent from the following considerations. Initially, the species present in the solution will be the aquo- (and/or acetato-) complexes of aluminium and copper, and a very small amount of the copper-PAN complex. Upon addition of EDTA the copper-EDTA complex will be formed first. If all the copper not blocked by the very stable PAN complex is titrated, EDTA will complex the more readily available aluminium. After all the aluminium is titrated, the copper will be taken from the indicator complex, and the end-point will occur when the sum of both metals is titrated. Hence, the stability of the indicator complex plays a decisive role. Thus the copper-PAN-EDTA system is used to indicate visually the end-point in the EDTA titration of many metals which do not form coloured compounds with PAN, and whose EDTA complexes are much less stable than that of copper, *e.g.*, calcium.[5]

Although stability constant data for metal-PAN complexes are not available, it appears from all experimental evidence that copper forms one of the most, if not the most, stable PAN complex. Suppose that instead of employing PAN as indicator, it is used as the titrant; then copper will be complexed preferentially in the presence of other metals. Here, step-indication is replaced by self-indication, with a consequent

* The term *photometric indicator* chosen by Underwood is correct. However, it may be confused with the general expression, *indicator in a photometric titration*, which includes step-indication. In order to avoid this possibility the term *slope indicator* is proposed. While it is true that detection of any end-point in a photometric titration is based on slope changes, the new term will not cause confusion when defined as above.

increase in selectivity. The use of PAN as titrant will be the subject of a further paper in this series.

Another example pertinent to the problem of selectivity is the EDTA titration of calcium using Erio T as indicator. The low absorptivity and low stability of the calcium-Erio T complex makes detection of the end-point exceedingly difficult. Biedermann and Schwarzenbach[6] pointed out that the addition of at least 5 mole % of magnesium makes possible a precise location of the end-point. However, only the sum of calcium plus magnesium is obtained, and to determine calcium the amount of magnesium added must be known exactly. (A more convenient approach, of course, is the addition of magnesium-EDTA complex). This is an example of step-indication with low selectivity. The selectivity can be increased by replacing step-indication by slope-indication. If any unknown amount of magnesium, and in addition an amount of Erio T is added more than equivalent to the magnesium, the situation is entirely changed. When EDTA is now added the stronger calcium complex will be formed first with only a slight change in absorbance. When all of the calcium is complexed, magnesium will be taken from the Erio T complex, this process being accompanied by a rather large change in absorbance. Thus the calcium end-point is obtained *via* the self-indicating system Mg-Erio T as the slope indicator. As in the case of example 4, only a few points of the Mg-Erio T portion of the titration curve are necessary to enable the determination of its slope. Although the determination of the magnesium present is entirely feasible here, it is irrelevant to the determination of calcium by the slope-indication method.

From this discussion, the significant difference between step- and slope-indication can readily be appreciated. In step-indication the *last* change in slopes is utilised, where the end-point for the titration of *both* metals occurs. In slope-indication the *first* change in slope, when the second metal starts to be titrated, is utilised, thus giving the end-point for the *first* metal only.

A practical application of the principles outlined above is the titration of magnesium in the presence of calcium using Erio T as the titrant. The calcium-Erio T complex is considerably weaker than that of the magnesium, and hence magnesium should complex first when Erio T is added as titrant. The progress of the titration can readily be followed photometrically.

When applying the theoretical considerations to practice, considerable difficulty is encountered because of the low storage stability of the dye. Unless special precautions are taken, a slight but steady drift in the galvanometer readings is observed, indicating decomposition of the dye. Hence, further experiments were performed with Calmagite. This dye, of similar constitution to Erio T,[7] shows practically identical behaviour in complex formation and colour developement, but has a superior storage stability. The stability constant of the magnesium complex[7] is $10^{5.69}$, which, for titrations in very dilute solutions, is too low to allow a well-developed titration curve. That this is true can be seen from the curves in Fig. 2. The curvature is so great that it is practically impossible to determine the slope of the first, supposedly straight, part of the titration curve when working at 620 mμ, the wavelength at which the metallised and unmetallised dye show the greatest difference in absorbance. This difficulty can be overcome by selecting 650 mμ. At this wavelength only the blue metallised form absorbs, though to a lesser degree. However, it is advantageous to titrate at this wavelength, because it is now unnecessary to determine the slope of the first part,

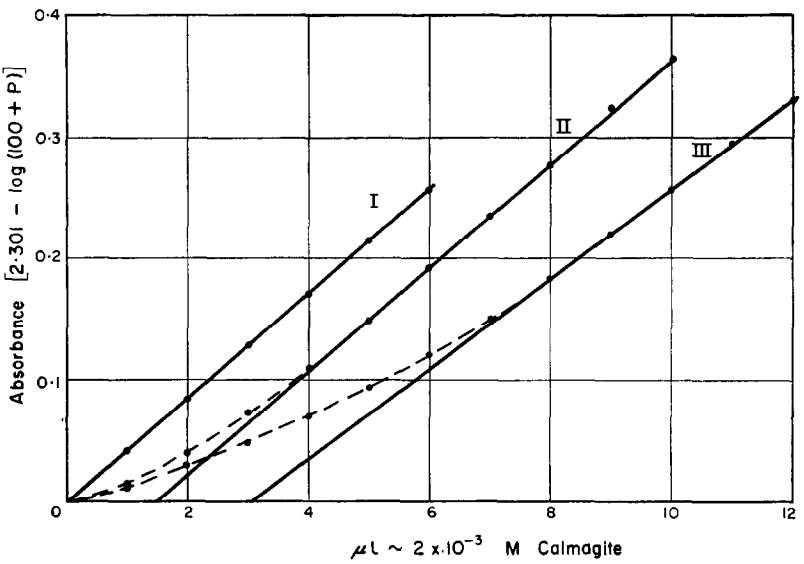


FIG. 2.—Titration of calcium and magnesium with $2 \times 10^{-3}M$ Calmagite solution. (0·5 ml of buffer pH 10: 649 mμ.)
(I) 50 μl of $5 \times 10^{-4}M$ calcium (Ca does not react); (II) 10 μl, and (III) 20 μl of $5 \times 10^{-4}M$ magnesium.

since it is known to be zero. It is only necessary to titrate with rather large increments until a region beyond the end-point is reached, where the titration curve is straight, and to extrapolate this line to the abscissa. Because a rather long portion of the titration curve is curved, the extrapolation must be carried out from far beyond the end-point, and this lowers the precision considerably.

It was shown that magnesium can be titrated in this way as a self-indicating system and that calcium does not interfere. But the results were not too impressive, and hence no further experiments were performed in this direction. Instead, the more promising possibility of adding excess dye to the sample solution and titrating with EDTA was investigated. Thus the self-indicating system, Mg-Calmagite-EDTA, was created, offering the additional possibility of being used as a slope indicator in the determination of calcium as mentioned above.

EXPERIMENTAL

All chemicals used were of highest available grade of purity. The water to make up the solutions was de-ionised water redistilled through a condenser made from a polyethylene tube.

Stock solutions of $0{\cdot}1M$ calcium, magnesium and EDTA were prepared, standardised complexometrically and diluted appropriately. The final calcium and magnesium solutions were $5 \times 10^{-4}M$; the titrant solution was $2{\cdot}18 \times 10^{-3}M$.

The buffer solution, pH 10, was prepared as follows: 1·14 ml of conc. ammonia, 140 mg of ammonium chloride and 50 mg of potassium cyanide were dissolved in 50 ml of high purity water.

For the dye solution, 20 mg of Calmagite were dissolved in 1 ml of water containing 1 drop of the buffer pH 10. For the daily supply of buffer containing dye, 5 μl of the dye solution were mixed with 5 ml of buffer. This procedure is recommended because in the strongly alkaline solution, over a period of days, the dye slowly fades. The dye titrant solution was prepared by dissolving 7 mg of Calmagite in 10 ml of high purity water. The corresponding solution was about $2 \times 10^{-3}M$.

Whenever possible plastic containers were used to handle and store solutions.

Apparatus: Ultramicro pipettes, calibrated "to contain", were used. The titration was performed with a Beckman/Spinco ultramicro burette, Model 153 A, with a total capacity of 0·12 ml and a precision of about ±0·01 μl. The original burette tip was slightly lengthened, and the holder for the titration vessel was replaced by a removable steel plate.

The photometer used in the present work has been described in Part II of this series.[8] Some minor modifications were necessary in order to adapt the instrument for the titration of small amounts of material. The 75-mm condenser lens was replaced by a smaller lens having a focal length of approximately 10 mm. Thus a light beam of nearly the same intensity, but with smaller diameter, was obtained, as is necessary when using very small titration vessels.

The titration cell was the bottom section cut from a chipped 1-cm Corex absorption cell originally used in a Beckman DU spectrophotometer. The cell was placed in a cell holder, shown in Fig. 3.

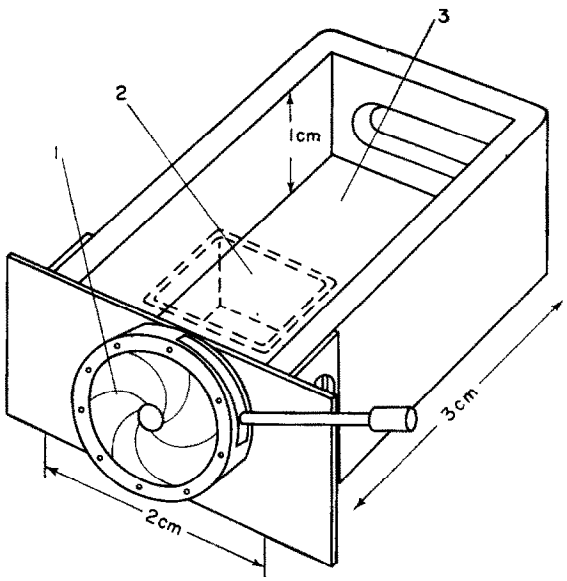


FIG. 3.—Holder for the micro titration cell: (1) iris diaphragm; (2) titration cell; (3) permanent magnet.

The holder was cemented together from sheets of Plexiglass cut to appropriate sizes. A small iris diaphragm was mounted on the front to allow adjustment of the light intensity. The titration cell was held in place by plastic wedges pressed between the side of the cell and the walls of the cell holder. The cell holder was cemented on a permanent magnet. Thus the cell assembly was held firmly on the steel plate of the titrator (see above) but still could be moved in order to obtain the best position within the light beam.

The titration assembly was positioned in the space between the lamp housing and the photoreceptor compartment of the titrator. The entrance opening of the photoreceptor compartment was provided with an aluminium plate having a small hole corresponding to the size and point of entry of the light beam (approximately 0·5 cm in diameter).

To permit shift of the scale (for theory, see later) a zero suppressor circuit was connected in series with the galvanometer and zero adjuster. The wiring diagram is shown in Fig. 4. Its operation is similar to that of the zero adjusting circuit discussed in an earlier paper,[8] with the exception that the variable resistance R_s allows a necessarily greater range of current to flow through the galvanometer. The resistance of this circuit is very low in comparison to that of the galvanometer damping resistor, and therefore the zero suppressor has a negligible effect on the damping and sensitivity of the galvanometer.

Procedure

(*a*) *With no zero suppression:* Place cell assembly in position and adjust zero on the galvanometer with no light reaching the photoreceptor. Place 0·500 ml of buffer containing the dye in the cell, and transfer the sample into the cell with a micropipette, rinsing several times with the buffer in the titration vessel. Insert stirrer and burette. Adjust 100 S.D. (scale divisions) via lamp rheostat and/or iris diaphragm. Titrate in small increments. Plot the results and evaluate in the usual way. For plotting modifications see theory in the following paragraph.

(*b*) *With zero suppression:* Place the cell assembly in position and adjust zero on the galvanometer with no light reaching the photoreceptor. Adjust 100 S.D. via the lamp rheostat and/or iris diaphragm.

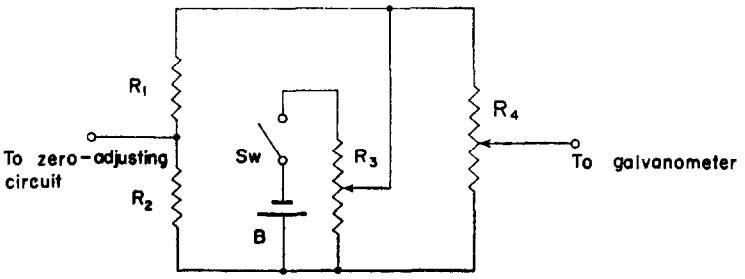


FIG. 4.—Wiring diagram of the zero suppressor: R_1 and R_2, 500 Ohms: R_3, 2·5 Megohms: R_4, 1000 Ohms: Sw, Switch: B, 1·35 volt mercury cell.

Switch on the zero suppression and adjust to zero S.D. by means of the zero suppressor controls.* Now no light reaches the photoreceptor and the pointer moves off scale to −100 S.D. (other values than −100 S.D. may be adjusted in an analogous fashion). Introduce the buffer and sample, insert the stirrer and burette and adjust to 100 S.D. with the initial solution as reference, using the lamp rheostat and/or iris diaphragm. Proceed as described under (*a*).

Higher precision methods

With a galvanometer reading from 0 to 100 the usual procedure, to set zero S.D. (= Scale Divisions) with no light reaching the photoreceptor and 100 S.D. with water as reference, is inconvenient for titrations involving solutions with a high initial absorbance. The portion of the galvanometer scale used during the titration may be very small even for large changes of absorbance. Adjustment to 100 S.D. with the initial solution is appropriate only when the absorbance increases during the titration. The precision of measurement is thereby increased by a factor of $100/T_i$, where T_i stands for the % transmittance of the initial solution, with water used as 100% T reference.

When the titration is accompanied by a decrease in absorbance the setting of 100 S.D. with the initial solution will result in a galvanometer deflection beyond that point. In order to benefit from increased precision, it is necessary in addition to shift the range of deflection in the negative direction. The possibility that some readings may still fall outside the galvanometer scale is dealt with later.

Discussion of a practical example will elucidate the above statements. In the EDTA titration of the self-indicating system Mg-Calmagite, the initial absorbance of the solution is approximately 1, mainly because of the presence of excess dye. Using water as reference to set 100 S.D., the galvanometer reading with the solution in the cell will be 10 S.D. When all the magnesium is titrated, more of the strongly absorbing dye is released and the final reading is, *e.g.*, 8 S.D. Although this corresponds to a change of approximately 0·1 absorbance unit, the galvanometer will have been deflected only 2 S.D. Obviously, under these conditions it is not possible to obtain sufficiently accurate readings for the construction of a usuable titration curve. When the initial solution is used to set the galvanometer to 100 S.D. (*e.g.*, by increasing the light intensity), the precision is increased by a factor of ten, because the 100% T point referred to water is at 1000 S.D. This instrumental manipulation does not, of course, affect the optical properties of the solution, and hence the change in absorbance is still 0·1 unit during the titration. However, the corresponding galvanometer deflection will be from 100 to 80 S.D.

* The setting of a certain zero suppression need be done once only. The selection of operation with or without zero suppression is readily handled by the switch in the zero suppressor circuit.

Heretofore in this discussion reference has been made mainly to galvanometer deflection which is proportional to transmittance; but to obtain a titration curve it is necessary to plot absorbance versus volume of titrant. The question arises whether it is a valid procedure to plot the negative logarithms of the galvanometer readings *versus* volume. The answer is readily obtained by applying a formula derived in a previous paper of this series.[8] Let M stand for the number of S.D. corresponding to zero transmittance (*i.e.*, no light reaching the photoreceptor). Let N stand for the number of scale divisions corresponding to 100% T set with water as reference, and P for the number of scale divisions read with the sample in the titration cell. Then the %T of the sample can be obtained from the following relation

$$(N - M):100 = (P - M):\%T \tag{1}$$

From this the absorbance is

$$A = -\log (\%T/100) = \log (N - M) - \log (P - M) \tag{2}$$

In the case now under discussion, zero transmittance corresponds to the zero point of the galvanometer scale, and hence $M = 0$. Thus the above expression for the absorbance simplifies to

$$A = \log N - \log P \tag{3}$$

Since log N (the numerical value need not be known) remains constant during any particular titration, plotting of log P (it is even not necessary to take account of the minus sign) *versus* volume of titrant is a valid procedure. Addition or subtraction of log N or any other constant results only in a shift of the titration curve in the direction of the ordinate, which, of course, does not influence the end-point read on the abscissa. Thus by subtracting log P from 2 it is readily ensured that the titration curve starts at the zero point of the ordinate.

If the galvanometer zero does not correspond to zero light intensity, $M \neq 0$. The first term on the right side of equation (2) is still constant during a particular titration; but plotting the logarithms of scale divisions is no longer a valid procedure. It is now necessary to plot log (P − M), and hence the value of M (in S.D.) must be known exactly. Regardless of the numerical value of M, it is still possible to subtract log (P − M) from any arbitrary constant in order that the titration curve again starts at the zero point of the ordinate.

If the zero is shifted to −100 S.D. (= M) and the initial solution is used to set 100 S.D., the logarithms of P − 100 are subtracted from 2.301 (= log 200) in order to start the titration curve at the zero point of the ordinate. It is convenient, when the setting $M = -100$ (or any other value) is used frequently, to prepare an appropriate table to facilitate the handling of results.

There are two cases in which M is not set equal to zero. First, such a setting may be used in order to achieve an increased precision in measurement. Second, it may be necessary to set M less than zero so that the galvanometer readings do not exceed 100 S.D. during the titration of a system in which the absorbance decreases.

The following example will show why an increased precision results. In the case discussed above, the setting of zero on the galvanometer scale was made with no light reaching the photoreceptor, and the setting of 100 S.D. was made with the initial solution. During the titration a galvanometer deflection from 100 to 80 S.D. was

observed. Suppose the galvanometer setting is adjusted to −100 S.D. with no light reaching the photoreceptor, by moving the scale, by applying an additional voltage, or by some other means. If, now, with the initial solution in the cell the setting is made to 100 S.D. (by increasing the light intensity), the galvanometer deflection during the titration will be from 100 to 60 S.D. Thus the precision with which the galvanometer can be read is doubled.

For a system whose absorbance decreases during the titration, the zero point (*i.e.*, the galvanometer setting with no light reaching the receptor) may, for example, be adjusted to −100 S.D. (= M). If the solution is now placed in the cell and the initial setting is made to be zero on the galvanometer scale (*via* change in light intensity), the galvanometer will deflect up the scale during the titration. When large changes in absorbance are involved, the pointer may still leave the galvanometer scale during the course of the titration. This can be avoided by decreasing the sensitivity through selection of a less negative value of M.

In order to find a suitable value for M, several pre-titrations may be necessary. To circumvent this inconvenience it is much simpler to operate with a sectioned titration curve. Whenever the pointer approaches 100 S.D. a re-setting to the zero point of the galvanometer scale is performed by changing the light intensity.

Sectioning the curve is also an appropriate procedure for a titration in which the absorbance increases. Whenever the pointer approaches the zero point of the galvanometer scale it is brought back to 100 S.D. by increasing the light intensity. An example of such a sectioned titration curve is shown in Fig. 5. A close inspection of

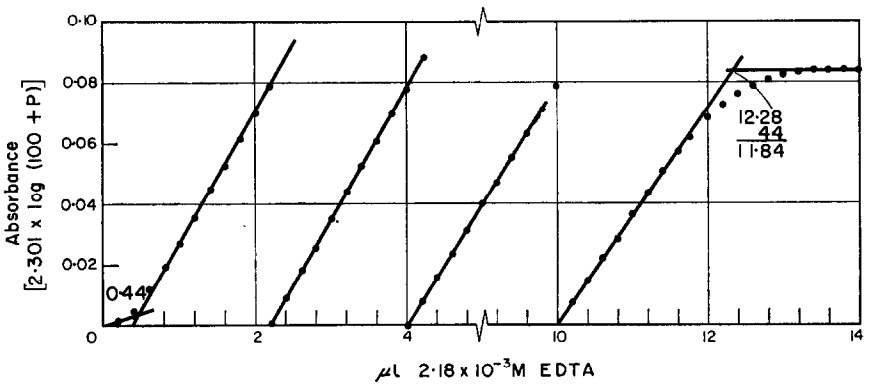


FIG. 5.—Dissection of a titration curve.
(50 μl of 5 × $10^{-4}M$ magnesium: 0·5 ml of buffer, pH 10: 622 mμ.)
The calcium blank is readily seen at the beginning of the titration curve.

the figure reveals that each succeeding section has a lower slope. This results from the dilution.

Correction for dilution

To correct for dilution generally, the absorbance values have to be multiplied by the factor F = (V + b)/V, where V is the initial volume and b the volume of titrant added. As discussed in the preceeding paragraph the titration curve results from a plot of −log (P − M) *versus* volume of titrant. In order to have the titration curve start conveniently at the zero point of the ordinate one may even plot R − log (P − M), where R is an arbitrary constant, as discussed for the case where the

absorbance increases during the titration. It is obvious that the correction factor has to be applied to the true absorbance, A, and not to the term, A′, which is actually plotted, and which for brevity, but incorrectly, is called absorbance.

From a comparison of the two equations,

$$A = \log (N - M) - \log (P - M)$$
$$A' = R - \log (P - M),$$

it can readily be seen that the application of the dilution factor to A′ only gives correct results when by chance $R = \log (N - M)$. The more the two terms differ numerically, the more incomplete is the correction. It is possible to determine the numerical value of the term $\log (N - M)$ and then to calculate the true absorbance and to apply the correction to it. However, this is highly inconvenient.

From these considerations, it follows that the most practical way is to employ titrant solutions with sufficiently high concentrations, obviating the necessity of applying a correction.

Blank and impurities

The smaller the amount of calcium and magnesium to be determined, the greater is the influence of impurities. It is hence essential to determine the magnitude of the blank and other corrections necessary with the highest possible accuracy. The magnitude of the blank varies greatly with each preparation of the buffer solution. In only one case was it possible to obtain a buffer solution free from a calcium blank. With appropriate care, however, one may keep the blank within reasonable limits.

Glass vessels for storage of solutions should be rejected, and only plastic containers should be used. When the use of a glass container is unavoidable (volumetric flasks) the contact time should be kept as short as possible. Special treatment of the containers before use is highly recommended (see later).

The main sources of extraneous calcium and/or magnesium are water and dust. De-ionised water has not been proven to be blank free. The most reliable water was obtained by distillation through a condenser made from a plastic tube. When such water is used to prepare the buffer solution only a very small blank can be observed initially. But after some time the blank may increase because of the introduction of calcium and/or magnesium from dust particles.

It is nearly impossible to obtain good results with the smallest amounts of metal ion titrated when the titration is performed in a room where smoking is permitted and many people are moving about. It is readily possible to obtain a correct titration curve up to a certain point and then to observe erratic readings when a dust particle falls into the solution. The erratic readings may not arise entirely from the optical interference caused by the particle. To eliminate this interference, the stirrer may be switched off and the reading made when the particle has left the region of the light beam. If the particle contains any titratable metal ion, erroneous changes in absorbance will deform the titration curve from that point on.

Besides being capable of introducing a chemical interference, dust is a nuisance because it is extremely tedious to wait after each addition of titrant for dust particles to leave the light beam, and with numerous and very small ones such a procedure becomes entirely impossible. Hence, freedom from dust is essential. Filtration is helpful in removing the particles, but very readily increases the blank considerably.

The most suitable filter medium is sintered-glass or porcelain boiled in conc. nitric acid and then treated with warm alkaline EDTA solution for several hours. Extensive rinsing with high-purity water follows the chemical treatment. The same treatment is necessary for the suction flask and the filter holder of the filter assembly. A plastic stopper is recommended for the filter outfit, since rubber particles are easily detached and are a ready source of metal ions. It is essential to bring the solution, after filtration, immediately from the filter flask to the plastic container for permanent storage.

Only small portions of buffer and other solutions should be transferred to a smaller plastic bottle for the daily supply, in order to avoid introduction of dust by too frequent opening of the bottle containing the main portion.

In order to check that the newly developed method would work, it was necessary to prepare calcium and magnesium solutions (in the present case $5 \times 10^{-4}M$ and $5 \times 10^{-5}M$) from more concentrated stock solutions, the molarities of the latter being determined by well-established complexometric procedures. Initial experiments revealed some trends in the results indicating a systematic error. The cause of that error was found in the fact that the water used for the preparation of the dilute solutions was not blank-free, and that calcium had been introduced into the magnesium solution and *vice versa*. These amounts had to be taken into account, and were determined in a similar fashion to the blank of the buffer solution. An example is shown in the results in Fig. 6. Clearly the value for magnesium increases with increasing calcium content. The amount of magnesium in this particular calcium solution was calculated from the results as being approximately equivalent to 0.05 μl of EDTA per 10 μl of the calcium solution. This series of experiments was performed in the initial phase of the investigation; later, with appropriate care, this type of impurity was maintained at a much lower level. In a practical calcium-magnesium analysis, correction for such impurities may become important, but only when standardising an extremely dilute solution of EDTA against an extremely dilute metal standard solution. With titrant concentrations of $0{\cdot}001M$ and higher, the standardisation need not be performed on the ultramicro scale; when large amounts of solutions are involved, the minute amounts of impurities do not cause interference. Using the results of Fig. 6, as collected and processed in Table I, the determination of the calcium blank in the buffer becomes evident.

There is a much simpler procedure for determining the calcium and magnesium blank of the buffer, in which the concentration of the calcium and magnesium

TABLE I.—PROCESSING OF THE RESULTS FOR DETERMINATIONS OF CALCIUM ACCORDING TO FIG. 2.

Given, μl $5{\cdot}07 \times 10^{-4}M$ Ca	5·00	10·0	20·0	30·0	40·0	50·0
Calculated, μl $2{\cdot}18 \times 10^{-3}M$ EDTA	1·15	2·29	4·59	6·88	9·18	11·47
Found, μl $2{\cdot}18 \times 10^{-3}M$ EDTA	1·40	2·56	4·86	7·12	9·40	11·76
Difference (= Blank)	0·25	0·27	0·27	0·24	0·22	0·29
μl EDTA corrected for blank (0·257)	1·14	2·30	4·60	6·86	9·14	11·50
Difference, μl EDTA (Corr.—Calcul.)	−0·01	+0·01	+0·01	−0·02	−0·04	+0·03
Difference, %	−0·88	+0·44	+0·22	−0·15	−0·44	+0·26

solutions involved need not be known. The procedure is as follows: A solution containing calcium and magnesium in about equimolar amounts is prepared, and a certain number of μl of this solution is transferred into the titration cell using 0·500 ml of buffer solution. The amount of metal solution should be such that sufficient titrant is required to allow the recording of a reliable titration curve. Several titrations

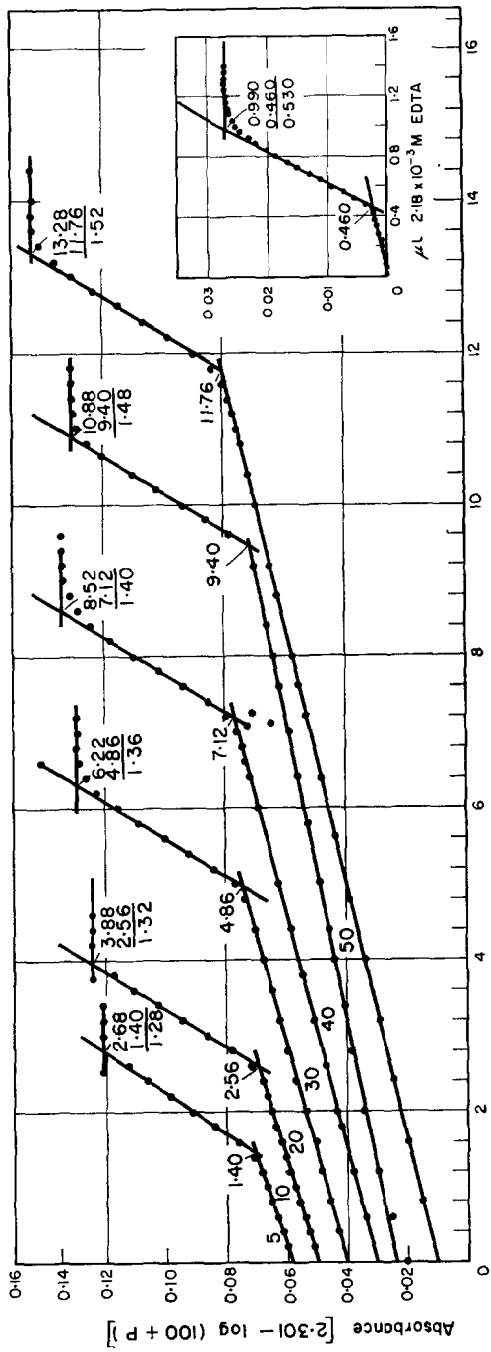


FIG. 6.—Titration of increasing amounts of calcium (5, 10, 20, 30, 40, 50 μl of $5 \times 10^{-4}M$) in presence of a constant amount (5 μl of $5 \times 10^{-4}M$) of magnesium. (0·5 ml buffer, pH 10: 622 mμ.)

Insert: Typical titration curve for very small amounts. 1 μl of Ca and 2 μl of Mg.

are performed using exactly the same amount of buffer and sample in each experiment. The results are averaged. Then another series of titrations is performed in exactly the same way, the only difference being that 1.00 ml of buffer is used. If any significant blank is present the corresponding results in the second series must be higher and the differences correspond to the blank value of calcium and magnesium respectively in 0.500 ml of buffer. A typical example is presented in Table II.

TABLE II.—TYPICAL DATA TO DETERMINE THE CALCIUM AND MAGNESIUM BLANK OF THE BUFFER

μl $2{\cdot}18 \times 10^{-3}M$ EDTA		μl $2{\cdot}18 \times 10^{-3}M$ EDTA	
For calcium	For magnesium	For calcium	For magnesium
using 0·500 ml buffer		using 1·00 ml buffer	
1·12	1·25	1·15	1·28
1·14	1·23	1·17	1·27
1·10	1·23	1·16	1·26
1·13	1·24	1·18	1·27
Average 1·122	1·238	1·165	1·270
A	B	C	D

Calcium blank per 0·500 ml buffer: C − A = 0·043 μl EDTA
Magnesium blank per 0·500 ml buffer: D − B = 0·032 μl EDTA

CONCLUSIONS

The determination of submicrogram quantities of calcium and magnesium with a surprisingly high precision and accuracy (Tables I and III) is readily achieved by evaluation of a single titration curve. The lower limits shown in this investigation are not the ultimate amounts titratable. With appropriate modifications of the titration cell, smaller amounts can be titrated as far as the sensitivity of the instrument and the readability of the burette will allow. However, a considerable increase in difficulties with sampling, purity of reagents, blank values and their constancy, dust, *etc.* will occur. No studies have been made with regard to interferences by other metals, because these can be predicted from the vast body of information about titrations on the micro and macro scale.

TABLE III.—TITRATION OF SMALL AMOUNTS OF $5 \times 10^{-4}M$ SOLUTIONS OF CALCIUM AND MAGNESIUM BY $2{\cdot}18 \times 10^{-3}M$ EDTA 0·5 ML OF BUFFER 10. 622 Mμ

Calcium					Magnesium				
μl	μg				μl	μg			
	given	found	diff.	Δ%		given	found	diff.	Δ%
1·00	0·0203	0·0200	−0·0003	−1·48	1·00	0·0122	0·0113	−0·0009	−7·38
2·00	0·0406	0·0425	+0·0019	+4·68	1·00	0·0122	0·0121	−0·0001	−0·82
3·00	0·0609	0·0585	−0·0024	−3·94	1·00	0·0122	0·0131	+0·0009	+7·38
4·00	0·0812	0·0803	−0·0009	−1·11	1·00	0·0122	0·0141	+0·0019	+15·6
5·00	0·1015	0·1036	+0·0021	+2·07	1·00	0·0122	0·0119	−0·0003	−2·46
1·00	0·0203	0·0203	−0·0001	−0·49	2·00	0·0244	0·0250	+0·0006	+2·46

It should be emphasised that the titration curves show a very low degree of curvature near the end-point. This seems surprising at first glance, when it is considered that the concentration of metal in the solution finally titrated is of the order of 10^{-7}–$10^{-6}M$ and that the stability constant of the magnesium-dye complex is only $10^{5 \cdot 69}$.[7] Since the dye is not used in relatively small quantities as an indicator, but is added in a considerable excess over the metal ions in order to create a self-indicating system, a very favourable shift of the equilibria, opposing the dissociation of the metal-dye complexes, is achieved. The curvature is considerably less than could otherwise be expected. With no excess dye, dissociation is large, as can be seen from the rather extensive curvature near the end-point in Fig. 2.

Since the handling of the samples and the operation of the instrument are simple compared with similar methods, practical application of these titrations seems feasible in many cases. For example, under the conditions described in this paper the titration of about 1 μg of calcium and 0.5 μg of magnesium present no difficulty in routine analysis, because in this range the effect of impurities and any blank is not serious. The amount of metals mentioned above correspond to those present in approximately 0·01 ml of blood serum. Thus, the two metals can readily be determined starting with one small drop of blood obtained from the finger. No puncturing of veins is necessary. Further, only one titration need be performed to determine both metals.

The principles developed here and tested experimentally are by no means restricted to the system calcium-magnesium. Any binary mixture of metal ions showing the appropriate optical and chemical behaviour can be treated in an analogous manner. A mixture of copper and zinc, *e.g.*, in the presence of excess PAN, could be titrated similarly with EDTA. There are even cases where one may determine three metals from one titration curve. Further examples are under investigation.

The principle applied here to small amounts of substances and to small volumes is not restricted to those conditions, and similar titrations may be performed with considerably higher amounts of material and in larger volumes. In some practical cases the solubility of the complexes, or the price of the dye may set the limit.

Acknowledgement—The work was performed under a grant of the National Science Foundation. Dr. F. Lindstrom supplied some of the new dye, Calmagite. This aid is gratefully appreciated.

Zusammenfassung—Drei verschiedene Typen von Endpunktsmechanismen bei photometrischen Titrationen, die auf Komplexbildung basieren, werden definiert und ihre Beziehung zum Selektivitätsproblem wird diskutiert. Einige der entwickelten Prinzipien werden auf die Bestimmung von Ultramikromengen Calciums und Magnesiums angewendet. Überschuss an Farbstoff (Calmagit) wird zu einer die beiden Metall enthaltenden, auf pH 10 gepufferten Lösungen zugesetzt, sodass die Metalle vollständig komplexiert sind. Die Titration wird mit ÄDTE durchgeführt. Eine Titrationskurve wird erhalten, die zwei Sprünge aufweist und somit gestattet beide Metalle in einem Zuge zu bestimmen. Änderungen an einem schon früher beschriebenen Phototitrator werden mitgeteilt und die dadurch erzielte Steigerung der Empfindlikeit und Präzision wird besprochen.

Résumé—Les auteurs définissent trois méthodes différentes de détection du point équivalent dans les titrages photométriques et discutent du problème de la sélectivité. Certains de ces principes sont appliqués au dosage du calcium et du magnésium en quantités allant jusqu'à quelques dixièmes ou quelques centièmes de microgrammes. Un excès de colorant (calmagite) est ajouté à la solution tamponnée à pH 10, contenant le calcium et le magnésium de sorte que ces deux métaux soient complexés. Ensuite le titrate est réalisée avec l'EDTA. On obtient ainsi une courbe de titrage avec deux points équivalents permettant la détermination de chaque métal présent. Les changements effectués dans un photomètre précèdemment décrit sont discutés, ainsi que l'accroissement de sensibilité et la précision.

REFERENCES

[1] P. B. Sweetser and C. E. Bricker, *Analyt. Chem.*, 1953, **25**, 253.
[2] K. L. Cheng and R. H. Bray, *ibid.*, 1955, **27**, 782.
[3] A. L. Underwood, *ibid.*, 1954, **26**, 1332.
[4] H. Flaschka and H. Abdine, *Z. analyt. Chem.*, 1956, **152**, 77.
[5] *Idem, Chemist-Analyst*, 1956, **45**, 58.
[6] W. Biedermann and G. Schwarzenbach, *Chimia*, 1948, **56**, 2.
[7] F. Lindstrom and H. Diehl, *Analyt. Chem.*, 1960, **32**, 1123.
[8] H. Flaschka and P. Sawyer, *Talanta*, 1961, **8**, 521.

Talanta, 1962, Vol. 9, pp. 265 to 269. Pergamon Press Ltd. Printed in Northern Ireland

THE ELECTROLYTIC OXIDATION OF OXALATE ION IN THE DETERMINATION OF CALCIUM AND MAGNESIUM

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Summary—A graphite anode has been found suitable for the electrolytic removal of excess oxalate ion following precipitation of calcium as oxalate and prior to determination of magnesium as phosphate or quinolate. Magnesium in concentrations as low as 5 mg in 250 ml of solution can be precipitated quantitatively when the solution is electrolysed for 20–30 min at 4 A. The method is applicable to limestone analysis according to the procedure of Kolthoff and Sandell.[1]

IN a procedure used for limestone analysis the precipitation of calcium oxalate is performed by neutralising with ammonia a hot hydrochloric acid solution containing a large excess of ammonium oxalate.[1]

High concentrations of oxalate render the precipitation of magnesium as the phosphate or quinolate incomplete because of the formation of complex ions. Quantities of ammonium oxalate of the order of 1 g in 100 to 200 ml do not interfere seriously.[2] Since a large excess of ammonium oxalate is employed in the precipitation of calcium, it must be destroyed before the determination of magnesium. Many textbooks maintain that oxalate can be destroyed by the use of concentrated nitric acid. A number of experiments have proved, however, that neither nitric acid nor *aqua regia* is a sufficiently strong oxidising agent for the destruction of oxalate ion.[3] Ammonium oxalate may be completely removed by volatilisation over a free flame after the solution is evaporated to dryness. Bromine has been found satisfactory for the oxidation of oxalate in aqueous solution and, although the procedure is laborious, it is probably the most time-saving method available.[3]

It has been found that 85% of the ammonium oxalate in a stirred acetic acid solution is oxidised in 30 min at cylindrical platinum gauze electrodes when the current is 1·5 A. The amount of ammonium oxalate remaining in solution is not sufficient to interfere with the precipitation of magnesium as phosphate or quinolate.

A number of tests indicated that graphite was suitable as an anode in a hydrochloric acid solution when the effective anode area was 160 cm^2 and the applied current was 4 A. More than 85% of the ammonium oxalate in a hydrochloric acid solution is destroyed in 25 min and the electrolysis is over 75% efficient at a simply fabricated sixteen rod graphite electrode. As shown in Fig. 1, the electrode requires no ring-stand or clamp and eliminates losses of solution caused by spattering. Experiments proved that magnesium can be precipitated quantitatively as phosphate and quinolate when the solutions are electrolysed for 20–30 min. Magnesium in concentrations as low as 5 mg in 250 ml of solution can be recovered and weighed as pyrophosphate.

Electrolytic removal of oxalate has been found applicable for the separation of calcium and magnesium in limestone analysis. After the removal of hydrous oxides, calcium is precipitated by neutralising a hydrochloric acid solution containing an

excess of ammonium oxalate. The solutions are electrolysed with stirring for 25 min at 4 A using the graphite electrode. The solutions are then filtered to remove any carbon particles which may be dislodged from the electrode surface and magnesium is precipitated as phosphate or quinolate.

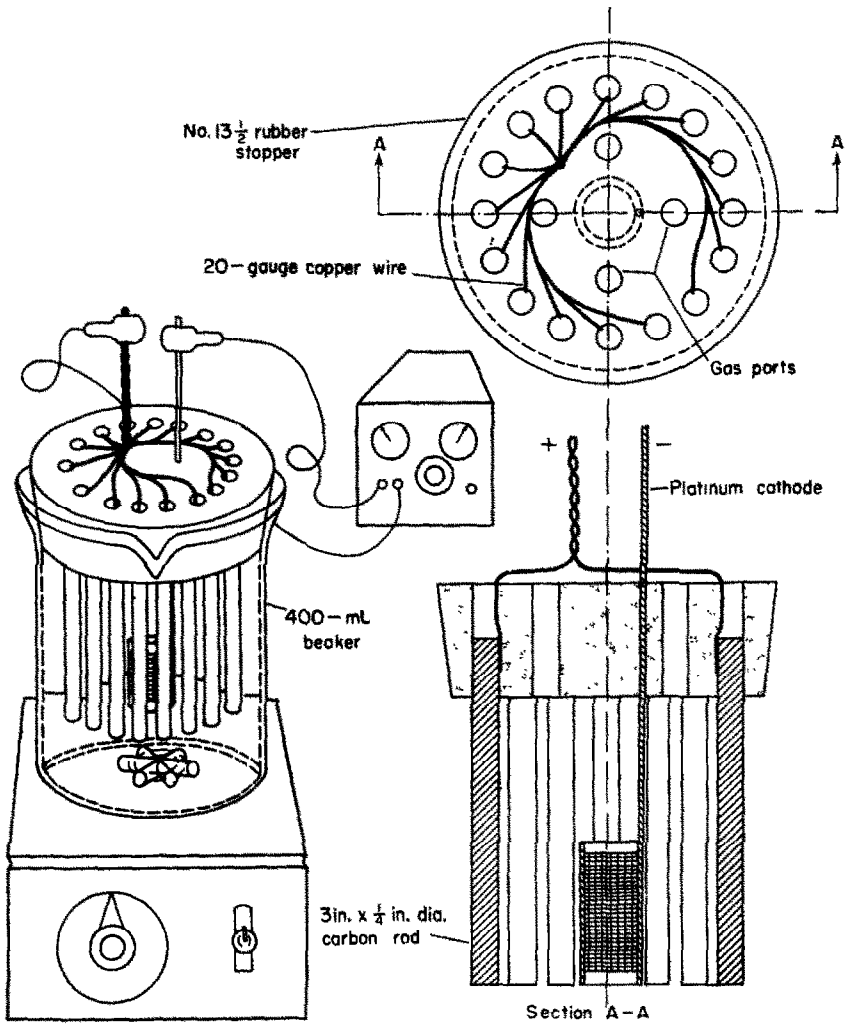


FIG. 1.—Sixteen rod graphite electrode assembly.

EXPERIMENTAL

The rectifier used as a source of direct current operated on 115 V of 60 cycle, single phase a.c. It furnished 25 A of rectified, filtered d.c. at 6 V with powerstat voltage control from zero to full voltage. Electrolysis time was measured with a stopwatch and solutions were stirred with a magnetic stirrer.

Electrolytic Oxidation of Oxalate

A number of coulometric experiments were performed in acetic acid and hydrochloric acid solutions to determine the efficiency and suitability of various electrodes as well as the time required for oxidation of a representative amount of ammonium oxalate. The composition of the experimental solutions corresponded approximately to that of solutions obtained from calcium oxalate precipitation

prior to magnesium determination. For precipitation in acetic acid solution 1·5 to 2 g of ammonium oxalate is used while 3 to 4 g is required in hydrochloric acid solution.

Oxidation in acetic acid solution

Seven solutions containing 50 ml of ammonium oxalate solution (40 g/l.), 10 ml of magnesium acetate solution (0·1 g of MgO/10 ml), 10 ml of glacial acetic acid and 125 ml of distilled water were prepared in beakers. The solutions were electrolysed for varying times at 1·5 A with platinum

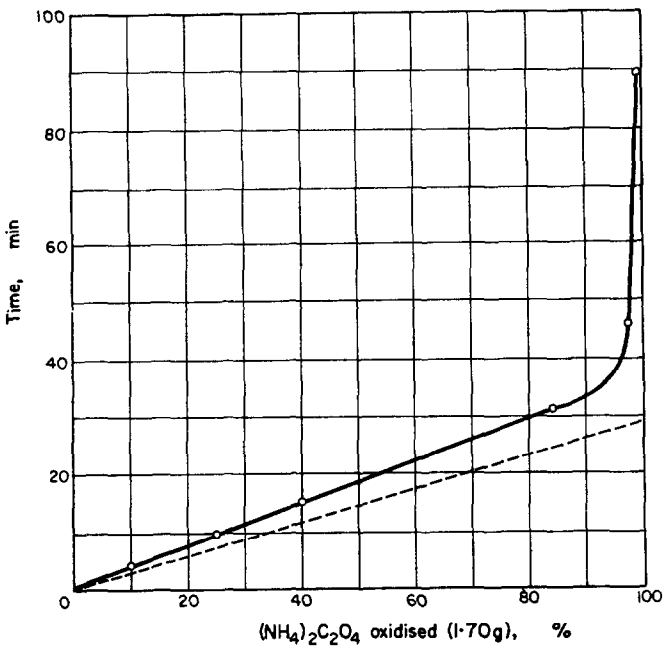


FIG. 2.—Efficiency of oxalate oxidation at platinum electrodes in acetic acid:
– – – theoretical (Faraday's law)
—○— experimental.

cylindrical gauze electrodes. The electrolysis was executed at room temperature with stirring. The weight of ammonium oxalate remaining after electrolysis was determined by titration with standard permanganate. The results (Fig. 2) indicate that 85% of the ammonium oxalate is oxidised in 30 min leaving approximately 0·25 g in solution which does not interfere appreciably with precipitation of magnesium ammonium phosphate or quinolate.

Oxidation in hydrochloric acid solution

Similar experiments were conducted in hydrochloric acid using electrodes other than platinum since it dissolves anodically. Solutions were prepared containing 100 ml of ammonium oxalate solution (40 g/l.), 10 ml of magnesium chloride solution (0·1 g of MgO/10 ml), 17 ml of concentrated hydrochloric acid, 12 ml of concentrated ammonium hydroxide and 150 ml of water. The solutions were electrolysed with stirring for varying times using graphite rod anodes in conjunction with a platinum cathode. The applied current was 4 A and the corresponding voltage was 5 V. Fig. 3 shows the effect of varying the current density by increasing the number of graphite rods. More than 85% of the oxalate was oxidised in 25 min with the sixteen rod anode and the electrolysis was over 75% efficient up to that point. The electrode did not disintegrate to any great extent and gas evolution was smooth.

Experiments were performed for the purpose of determining the time that the solutions should be electrolysed in order to obtain a quantitative precipitation of magnesium as phosphate or quinolate. Solutions with the same composition as in the previous experiment were prepared and electrolysed for varying times at 4 A with stirring at the sixteen rod graphite anode. After electrolysis the electrodes were rinsed thoroughly with distilled water and the solutions were filtered to remove the few carbon particles which were dislodged from the electrode. Magnesium was then precipitated and determined

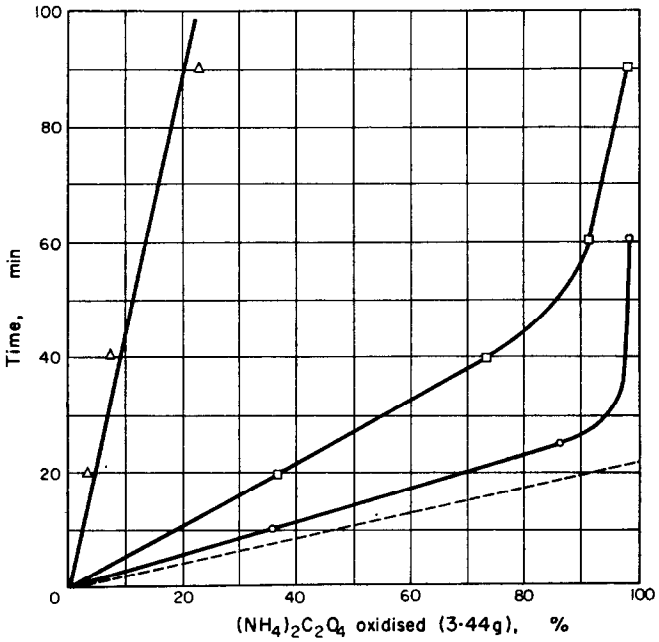


FIG. 3.—Oxidation efficiency at graphite electrodes in hydrochloric acid:
– – – theoretical (Faraday's law)
—△— single rod graphite anode
—□— eight rod graphite anode
—○— sixteen rod graphite anode.

TABLE I.—DETERMINATION OF MAGNESIUM WITH VARYING TIMES OF ELECTROLYSIS

Time of electrolysis, *min*	$(NH_4)_2C_2O_4$ present, *g*	Magnesium found* as pyrophosphate, *g*	Magnesium found* as quinolate, *g*
10	2·20	0·0537	0·0464
10	2·20	0·0540	0·0472
20	0·98	0·0545	0·0539
20	0·98	0·0545	0·0543
30	0·10	0·0546	0·0544
30	0·10	0·0545	0·0540

* 0·0545 g of magnesium present.

TABLE II.—DETERMINATION OF MAGNESIUM IN LIMESTONES

Thorn-Smith Sample No.	Magnesium oxide present, %	Magnesium oxide found as pyrophosphate, %	Magnesium oxide found as quinolate, %
71(a)	4·19	4·26	
71(b)	4·19		4·15
78(a)	10·97	11·08	
78(b)	10·97		10·99
90(a)	21·61	21·48	
90(b)	21·61		21·60

as phosphate and quinolate. Results shown in Table I indicate that precipitation is quantitative when the solutions are electrolysed for 20–30 min.

An investigation was carried out to ascertain if variable quantities of magnesium could be determined quantitatively after the solutions were electrolysed for 25 min. Results indicated that as little as 5 mg of magnesium can be detected as the pyrophosphate.

Finally the results of the analysis of three limestone samples in which the excess oxalate was destroyed electrolytically showed (Table II) that the subsequent determination of magnesium is quantitative.

Zusammenfassung—Der Ueberschuss der Oxalationen, der von der Bestimmung des Kalziums als Kalziumoxalat herruehrt, kann elektrolytisch zerstoert werden u.zw. mit Hilfe einer Graphit-elektrode. Dies ist in der Regel notwendig vor der Bestimmung des Magnesiums entweder als Phosphat oder Oxinat. Magnesium in einer Konzentration von fuenf Milligramm per 250 Milliliter kann noch quantitativ gefaellt werden, wenn die Loesung vorher durch 25–30 Minuten mit einem Strom von 4 Ampère elektrolysiert wurde. Diese Arbeitsweise kann zur Analyse des Kalksteines verwendet werden nach der Methode von Kolthoff und Sandell.

Résumé—On a découvert une anode de graphite pour détruire par l'électrolyse l'excédent des ions d'oxalate à la suite de la précipitation du calcium pour former de l'oxalate et avant la résolution du magnésium en phosphate ou quinolate. Le magnésium dans des concentrations même de la faiblesse de 250 ml. peut se précipiter quantitativement si on électrolyse la solution de vingt à trente minutes à quatre amperes. Cette méthode peut s'appliquer à l'analyse de la pierre de chaux selon le procédé de Kolthoff et Sandell.

REFERENCES

[1] I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, Macmillan Company, New York, 1952, p. 349.
[2] *Idem, ibid.*, p. 360.
[3] T. Holth, *Analyt. Chem.*, 1949, **21**, 1225.

Talanta, 1962, Vol. 9, pp. 271 to 284. Pergamon Press Ltd. Printed in Northern Ireland

OXIDIMETRIC DETERMINATION OF ORGANIC COMPOUNDS BY MEANS OF STRONG OXIDISING AGENTS

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Summary—A survey of the complete oxidation in aqueous solutions of organic compounds by means of strong oxidising agents is presented. A discussion of the influence of acidity and of the possibilities of working at higher temperatures are given, as well as some general remarks for further research in this field.

INTRODUCTION

OF the various types of chemical reactions that may underlie a titrimetric determination, oxidation-reduction reactions are the most important, especially those reactions in which the substance to be determined is oxidised by the reagent.

Although in organic chemistry titrimetric analysis, in general, is less important than in inorganic chemistry, because of the smaller rate of the reactions, still many attempts have been made to develop titrimetric procedures for the determination of organic compounds. It is the aim of this review to collect the most important results obtained in oxidimetric analysis of organic compounds and to discuss them in a critical way in order to obtain some lines of conduct for fruitful further investigations in this field of analysis.

Two types of oxidation of an organic compound can be distinguished:

(1) Moderate oxidation by a moderate or sometimes a strong oxidising agent.
(2) Complete oxidative breakdown *e.g.* into carbon dioxide and water. These reactions can only be carried out by means of very strong oxidising agents.

As the first example of the moderate type of oxidation may be mentioned some recently published oxidimetric determinations by means of vanadium^{V}, belonging to the half reaction:

$$VO_2^+ + 2H^+ + e \rightleftarrows VO^{2+} + H_2O$$

with a normal potential of 1·00 V at pH = 0.[1] In strong sulphuric acid solutions West and Skoog[2] determined α-hydroxy acids by means of oxidation with vanadium^{V} to the corresponding carboxylic acid with one carbon atom less and carbon dioxide. Rao *et. al.*[3] described a similar determination of α-amino acids after prior de-amination. They claim the formation of formic acid instead of carbon dioxide. The determination of uric acid by means of oxidation with vanadium^{V} to alloxan is described by Rao and Murty.[4]

A second example is the well-known "Malaprade" reaction, the determination of α-diols, α-diketones and similar compounds by means of potassium periodate.[5] At room temperature in approximately neutral solution these organic compounds are stoichiometrically oxidised within a few min, *e.g.* in the case of α-diols by means of a cleavage of the C—C bond between the carbon atoms that bear the hydroxyl groups

and formation of the respective aldehydes. Periodate is reduced to iodate according to the half reaction:

$$H_5IO_6 + H^+ + 2e \rightleftarrows IO_3^- + 3H_2O.$$

Although the normal potential of the periodate-iodate couple is 1.6 V at pH = 0, and periodate is, therefore, a very strong oxidising agent, the oxidation does not proceed beyond the aldehyde state. Thus it is a moderate oxidation by means of a very strong oxidising agent.

A third and last example of these moderate oxidations is the excellent determination of formaldehyde by oxidation to formate in alkaline solution by the strong oxidising reagent hypoiodite, according to Romijn.[6]

These examples of moderate stoichiometric oxidations are a completely arbitrary choice. There are a number of other reactions of the same type in use in titrimetric organic analysis. It is not the aim of this review, however, to sum up all reactions of this type, because it is not possible to do it in a systematic way.

Every oxidising agent has its own typical aspects and it is better in this respect to review the reactions of each oxidising agent; this has been carried out in some textbooks[7,8] and in some reviews.[9,10]

The main difficulty in moderate oxidations, as mentioned above, is that the reactions are, in general, not stoichiometric and that very often empirical factors are needed for obtaining correct results. This lack of stoichiometry does not occur in oxidations of the second type, *i.e.*, complete oxidative breakdown, usually to carbon dioxide and water. This type of oxidation can only be carried out by means of very strong oxidising agents. Accordingly, this review is limited to this second type of oxidation in aqueous solution. The various strong oxidising reagents will be compared with respect to this type of reaction and the influence of the acidity of the solution on the oxidation of organic compounds will be discussed.

SURVEY OF THE VARIOUS STRONG OXIDISING REAGENTS

From the thermodynamic point of view the strength of an oxidising reagent is determined by the normal potential of the half reaction combining the oxidising reagent and the substance to which it is reduced.

As is well known, it must be realised that the rate of a thermodynamically possible oxidation-reduction reaction may be and is, in many cases, negligible, especially the oxidation of organic compounds. Although the rate of oxidation of any compound is by no means related to the oxidation potential of the oxidising reagent involved, oxidative breakdown of organic compounds is, in general, exclusively brought about by very strong oxidising agents, although the opposite, of course, does not hold. Therefore, we can limit ourselves in the second type of oxidation of organic compounds to oxidations by means of very strong oxidising agents and only to those oxidising agents which are stable in aqueous solution, preferably also at higher temperatures.

The normal potential of the majority of half reactions strongly depends on the acidity of the solution. Therefore a distinction will be drawn between very strong oxidising agents in acidic and in alkaline solution.

An oxidising agent will be called a very strong oxidising agent when it belongs to a half reaction having a normal potential $> 1{\cdot}3$ V at pH = 0 or of $> 0{\cdot}3$ V at pH = 14.

There is still another important reason to distinguish between redox reactions in acidic and alkaline solution, because the rate of these reactions frequently depends strongly on the acidity of the solution.

A great number of compounds, organic as well as inorganic compounds, are exclusively or preferably oxidised in either alkaline or acidic solution, *e.g.*

(1) Hydrogen cyanide is stable towards strong oxidising agents in an acidic medium. In neutral and alkaline solutions quantitative oxidation to cyanate takes place fairly rapidly.
(2) Oxidation of formic acid is only very slow in an acidic medium; in an alkaline medium quantitative determinations can be carried out by means of oxidation of formate to carbon dioxide and water.
(3) Oxalic acid behaves in an exactly opposite manner. In alkaline solution no oxidation occurs, in an acidic medium a quantitative determination by means of oxidation to carbon dioxide and water can be carried out with several strong oxidising agents.

In order to see which oxidising agents have to be considered in oxidations of the second type, those half-reactions that have the qualifications mentioned above are listed in Tables I and II. Table I refers to half-reactions in an acidic medium and corresponding normal potentials at pH = 0, whilst Table II does the same for alkaline solutions and pH = 14. The values given are those recorded by Latimer.[1]

TABLE I

Half reaction		E_0, *V*
$H_2O_2 + 2H^+ + 2e$	$\rightleftarrows 2H_2O$	1·77
$MnO_4^- + 4H^+ + 3e$	$\rightleftarrows MnO_2 + 2H_2O$	1·69
$HClO_2 + 2H^+ + 2e$	$\rightleftarrows HClO + H_2O$	1·64
$HClO + H^+ + e$	$\rightleftarrows 0{\cdot}5Cl_2 + H_2O$	1·63
$Ce^{4+} + e$	$\rightleftarrows Ce^{3+}$	1·61
$H_5IO_6 + H^+ + 2e$	$\rightleftarrows IO_3^- + 3H_2O$	1·60
$HBrO + H^+ + e$	$\rightleftarrows 0{\cdot}5Br_2 + H_2O$	1·59
$BrO_3^- + 6H^+ + 5e$	$\rightleftarrows 0{\cdot}5Br_2 + 3H_2O$	1·52
$MnO_4^- + 8H^+ + 5e$	$\rightleftarrows Mn^{2+} + 4H_2O$	1·51
$Mn^{3+} + e$	$\rightleftarrows Mn^{2+}$	1·51
$HIO + H^+ + e$	$\rightleftarrows 0{\cdot}5I_2 + H_2O$	1·45
$Cl_2 + 2e$	$\rightleftarrows 2Cl^-$	1·36
$Cr_2O_7^{2-} + 14H^+ + 6e$	$\rightleftarrows 2Cr^{3+} + 7H_2O$	1·33

TABLE II

Half reaction		E_0, *V*
$ClO^- + H_2O + 2e$	$\rightleftarrows Cl^- + 2OH^-$	0·89
$HO_2^- + H_2O + 2e$	$\rightleftarrows 3OH^-$	0·88
$BrO^- + H_2O + 2e$	$\rightleftarrows Br^- + 2OH^-$	0·76
$H_3IO_6^{2-} + H_2O + 2e$	$\rightleftarrows IO_3^- + 3OH^-$	0·70
$ClO_2^- + H_2O + 2e$	$\rightleftarrows ClO^- + 2OH^-$	0·66
$BrO_3^- + 3H_2O + 6e$	$\rightleftarrows Br^- + 6OH^-$	0·61
$MnO_4^{2-} + 2H_2O + 2e$	$\rightleftarrows MnO_2 + 4OH^-$	0·59
$MnO_4^- + e$	$\rightleftarrows MnO_4^{2-}$	0·56
$IO^- + H_2O + e$	$\rightleftarrows I^- + 2OH^-$	0·49
$Fe(CN)_6^{3-} + e$	$\rightleftarrows Fe(CN)_6^{4-}$	0·36
$ClO_4^- + H_2O + 2e$	$\rightleftarrows ClO_3^- + 2OH^-$	0·36
$ClO_3^- + H_2O + 2e$	$\rightleftarrows ClO_2^- + 2OH^-$	0·33

In the remaining part of this section the results obtained in oxidations of organic compounds by means of the oxidising agents included in Tables I and II will be briefly mentioned, especially with respect to oxidations of the second type *viz.* complete breakdown of organic compounds. Only those aspects of the oxidising agents necessary for a comparative discussion of these reagents later in this paper will be mentioned. For a complete picture of the applications of every reagent, reviews and textbooks are available.[7,8,9,10]

Hydrogen peroxide

Although hydrogen peroxide is a very strong oxidising agent in an acidic as well as in an alkaline medium and although it is under certain conditions fairly stable in aqueous solutions at room temperature so that a few quantitative determinations of inorganic compounds appear to be possible,[11,12] it will not be possible to carry out any quantitative oxidation of a more complicated character with this reagent. For, hydrogen peroxide is unstable with respect to its own disproportionation into oxygen and water, which is evident from the half-reactions:

$$H_2O_2 + 2H^+ + 2e \rightleftarrows 2H_2O \quad \text{with} \quad E_0 = 1{\cdot}77 \text{ V at pH} = 0$$
$$H_2O_2 \rightleftarrows O_2 + 2H^+ + 2e \quad \text{with} \quad E_0 = 0{\cdot}68 \text{ V at pH} = 0$$

and similar half reactions in alkaline media.

Although under certain conditions this disproportionation only takes place at an extremely small rate, it will give rise to loss of oxygen and thus to titration errors when the time for an oxidation becomes long or when reactive intermediates occur or when heating is necessary for a completely stoichiometric oxidation.

Halogens, their oxyacids and their oxyanions

The halogens, their oxyacids and their oxyanions belong, in acidic as well as in alkaline solution to the strong oxidising agents as is clear from Tables I and II. Because of the many disproportionation reactions taking place and because in many of the half reactions involved more than one of these compounds occur, it is best to treat these compounds together.

Chlorine, oxyacids and oxyanions of chlorine

To Table I the following half reactions can be added:

$$ClO_4^- + 2H^+ + 2e \rightleftarrows ClO_3^- + H_2O \qquad E_0 = 1{\cdot}19 \text{ V at pH} = 0,$$
$$ClO_3^- + 3H^+ + 2e \rightleftarrows HClO_2 + H_2O \qquad E_0 = 1{\cdot}21 \text{ V at pH} = 0.$$

From Tables I and II and the two half reactions mentioned above a number of important conclusions can be drawn.

Although from a thermodynamic point of view perchlorate and chlorate ions are strong oxidising agents in alkaline solution, the reactivity of these ions in this medium, as well as in an acidic medium, is very poor, *e.g.* perchlorate ion is only reduced at a very slow rate in an acidic medium by such a very strong reducing agent as chromium^{II}. Chlorous acid and chlorite ions are more reactive and recently quantitative oxidations of some compounds by means of chlorite have been examined by Minczewski and Glabisz.[13] Although it is possible that chlorites and chlorous acid may be valuable oxidising agents in some cases, the authors feel that for the complete oxidation of

organic compounds, hypochlorous acid and hypochlorites are to be preferred not only from the thermodynamic but also from the reactivity point of view.

Hypochlorous acid in acidic solution and hypochlorite ion in alkaline solution are very strong oxidising agents. Both are thermodynamically unstable with respect to disproportionation to chlorine and chlorate and perchlorate ions in acidic solution, and to chloride ion on the one hand and to chlorate and perchlorate ions on the other in alkaline solution. However, these disproportionation reactions are slow and, under ordinary conditions, do not pass beyond the chlorate state so that the reaction will not necessarily give rise to titration errors when using hypochlorous acid or hypochlorite in titrimetric analysis, because in a back titration all chlorine compounds left can be brought to the chloride state without any loss of oxygen.

There is, however, a decomposition reaction that can cause serious errors namely:

$$2HClO \rightleftarrows 2H^+ + 2Cl^- + O_2$$

which takes place in acidic and in alkaline solution. Pierron[14] showed that the decomposition caused by this reaction increases in the order: LiOCl, NaOCl, KOCl. In all cases the rate of decomposition reaches a minimum in neutral solution, but even then the decomposition is from 5 to 25% when the solutions are heated for a few hr at 100°. Although this decomposition reaction is very slow and even negligible under less extreme conditions, *e.g.* room temperature, it looks as if it is responsible for the fact that no complete oxidations of organic compounds by hypochlorite or hypochlorous acid are described in the literature. Only several simple quantitative oxidations by means of these reagents are known.[15,16] More complex oxidation reactions with these reagents do not seem to take place at an appreciable rate at room temperature, although some further research on this subject is warranted, especially in an alkaline medium and perhaps particularly in lithium hydroxide solution, because there are few strong oxidising agents in alkaline medium.

Bromine, oxyacids and oxyanions of bromine

To Table I the following half reaction can be added:

$$0{\cdot}5Br_2 + e \rightleftarrows Br^- \quad \text{with} \quad E_0 = 1{\cdot}065\ V.$$

The stable oxidising compounds of bromine are less in number than those of chlorine. Bromate acts in an acidic and in an alkaline solution as oxidising agent, hypobromous acid in an acidic solution only, hypobromite in an alkaline solution and elementary bromine in an acidic solution, the latter being only a moderate oxidant.

Bromate, although belonging to a half reaction with a large normal potential in acidic and in alkaline media, is only slightly reactive.[10] It is often used in an acidic medium together with bromide ions and it then acts as elementary bromine which shows a greater reactivity than bromate, but it has scarcely any significance in organic oxidimetry.

Hypobromous acid and hypobromites are strong oxidising agents. They have lower oxidation potentials than the corresponding chlorine compounds but, in general, they show a greater reactivity. They are also less stable than the corresponding compounds of chlorine. This means that in oxidation processes that require much time or that have to be carried out at higher temperatures, oxygen losses will make a quantitative analysis impossible.

The best results are obtained by means of the chlorine compounds to which bromide ions are added, in which case the solutions act as solutions of hypobromous acid or hypobromites.[17,18,19]

The authors feel that in an acidic medium there is no place for this reagent besides the well known stable oxidimetric reagents, but that hypobromite may be of value in alkaline solution in simple oxidation processes, although up to the present hardly any applications of bromine compounds are known in oxidimetric organic analysis.

Iodine, oxyacids and oxyanions of iodine. Only two valency states of iodine act as strong oxidising agents, in acidic as well as in alkaline solution.

Hypo-iodous acid and the hypo-iodites are for the same reasons as in the cases of the corresponding chlorine and bromine compounds unsuitable for oxidations at higher temperatures or of long duration. Some quantitative processes in an alkaline medium are known, however, including a few oxidations of organic compounds *e.g.* aldehydes.[6,20]

Periodate and periodic acid have already been mentioned in the *Introduction*. These compounds are of interest in a great number of specific oxidations of organic compounds, *e.g.* "Malaprade" reactions.[3] No applications are known, however, of further stoichiometric oxidations of organic compounds by means of these reagents.

Higher valency states of manganese

Tervalent, sexavalent and heptavalent manganese are very strong oxidising agents either in acidic or in alkaline solution, or in both of them.

Manganese^{III} is of no practical importance in quantitative analysis. Apart from its stability in a few complexes, when it is no longer a strong oxidising agent, it only shows any definite stability in strongly acidic solutions and then insufficient for practical purposes.

The discussion will, therefore, be restricted to manganate and permanganate. The half reactions in which these two ions take part are summarised below:

$MnO_4^- + 8H^+ + 5e \rightleftarrows Mn^{2+} + 4H_2O$	$E_0 = 1{\cdot}51$ V	in acidic solution at pH = 0,
$MnO_4^- + 4H^+ + 3e \rightleftarrows MnO_2 + 2H_2O$	$E_0 = 1{\cdot}69$ V	
$MnO_4^- + e \rightleftarrows MnO_4^{2-}$	$E_0 = 0{\cdot}564$ V	in alkaline solution at pH = 14.
$MnO_4^- + 2H_2O + 3e \rightleftarrows MnO_2 + 4OH^-$	$E_0 = 0{\cdot}588$ V	
$MnO_4^{2-} + 2H_2O + 2e \rightleftarrows MnO_2 + 4OH^-$	$E_0 = 0{\cdot}600$ V	

In alkaline solution it is seen that at pH 14 three half reactions are possible. In solutions of lower alkalinity the normal potential of the permanganate–manganate couple does not change, while the other two normal potentials rise, the result being that with decreasing alkalinity manganate becomes thermodynamically unstable with respect to disproportionation to permanganate and manganese dioxide. The actual behaviour of manganate solutions is in accordance with these calculations. Manganate is only stable in solutions more than 1*M* in alkali hydroxide. At lower alkalinities disproportionation of manganate takes place, increasing in rate with decreasing alkalinity. Therefore, permanganate is the only strong oxidising agent of manganese of practical importance in an acidic solution. It takes part in two half reactions, one producing manganese dioxide and occurring in slightly acidic solution, the other proceeding to manganese^{II} and taking place at higher acidities.

The significance of manganate and permanganate will be discussed separately.

Permanganate. Permanganate is the best known strong oxidant. It owes its important place in analytical chemistry to several excellent properties: it can easily be obtained, it is intensely coloured, it is a very strong oxidising agent in both acidic and alkaline solution from the thermodynamic (normal potentials of the half reactions in question) and from the reactivity point of view. One of the most important properties of a reagent to be used in oxidimetric analysis, *viz.* stability under various conditions, will first be discussed. Especially in oxidation processes taking up much time or requiring higher temperatures, oxidant stability is of great importance. Permanganate solutions are most stable in neutral solution. The addition of manganese^{II} or manganese dioxide, increasing acidity and rise in temperature decrease the stability of permanganate solutions. Some experimental evidence is given in Table III.

TABLE III

Expt.	Initial permanganate concentration, *M*	Acidity	Temp., °C	Time	Decompn., %
1	0·01	neutral	100	1 hr	0·0
2	0·002	neutral	100	1 hr	1·0
3	0·01 (Mn^{II}*)	neutral	100	1 hr	0·4
4	0·01	neutral	20	1 year	0·0
5	0·01	0·2*M* H_2SO_4	20	24 hr	0·7
6	0·01 (Mn^{II}*)	0·2*M* H_2SO_4	70	1 hr	10

* Mn^{II} was added in experiments 3 and 6, causing formation of MnO_2.

Summarising, to avoid titration errors in titrimetric procedures involving permanganate in an acidic medium and taking much time, it is absolutely necessary to work at low acidities and at room temperature. Without manganese^{II} or manganese dioxide being present these conditions would not be stringent, but in oxidations with permanganate these compounds are formed directly from the beginning of the process.

In alkaline solution the behaviour of permanganate is different. The stability of permanganate now depends on the alkalinity of the solution, the permanganate concentration, the temperature and the time. Manganese dioxide does not influence the stability of alkaline permanganate solutions.

Several investigations[23,24,25,26] dealing with this stability have been carried out. It was found that the decomposition of alkaline solutions of permanganate is exclusively caused by the reaction:

$$4MnO_4^- + 4OH^- \rightarrow 4MnO_4^{2-} + O_2 + H_2O.$$

As already stated, at lower alkalinities manganate shows a disproportionation but this is a reaction without loss of oxygen and it does not, therefore, result in titration errors.

The extent to which an alkaline permanganate solution is converted to manganate is outlined in Table IV.

The main characteristics for the decomposition from this table and also from a great number of other decomposition experiments[23,24,25,26] are:

(1) Decomposition is very large in the beginning. When a certain amount of manganate is formed, the decomposition decreases markedly (expt. 1 and 2).

(2) Decomposition increases with decreasing initial concentration of permanganate (expt. 3, 4 and 5).

(3) Decomposition increases with increasing alkalinity (expt. 4 and 6).
(4) Decomposition increases with increasing temperature (expt. 1 and 3).

Elimination of titration errors in titrimetric procedures involving alkaline permanganate only seems possible at room temperature, at low alkali hydroxide concentration ($< 1M$) and at large permanganate concentration ($> 0{\cdot}1M$ permanganate). After this discussion of the stability of permanganate solutions a survey of the most important investigations on titrimetric procedures involving strong oxidations of organic compounds by means of permanganate is given. Only those investigations will be mentioned which present a new aspect to this field.

The application of permanganate to quantitative analysis dates from 1846[27] and in the next 80 years a great number of analyses, including that of organic compounds, has been described, *e.g.* those by Péan de St. Gilles[28] and Lenz.[29] Some authors reveal

TABLE IV

Expt.	Initial permanganate concentration, M	Alkali hydroxide concentration, M	Time, *hr*	Temp., °C	Decompn. into manganate, %
1	0·01	1	2	20	4
2	0·01	1	48	20	4
3	0·03	2	1	35	10
4	0·003	2	1	35	25
5	0·0003	2	1	35	60
6	0·003	4	1	35	70

their knowledge of the sometimes essentially different behaviour of some compounds towards oxidation in alkaline and acidic media, but the investigators have not, in general, succeeded in developing stoichiometric determinations of organic compounds and only carry out quantitative analysis of more complicated organic compounds by using empirical factors. The first to state that oxidimetric processes with permanganate taking much time should be carried out at room temperature was Kolthoff.[21] Subsequently, Imhof[30] carried out a systematic investigation of the oxidation of many organic compounds, mainly to carbon dioxide and water, by permanganate in acidic and in alkaline media at room temperature. He also indicated that in many cases it is of great value to begin an oxidation in an alkaline medium, then to continue for a certain time in an acidic medium.

Imhof collected much valuable data about oxidisibility of organic compounds in acidic and alkaline solutions and also obtained a number of correct results for quantitative analysis according to his procedures. The main drawbacks to Imhof's methods are that his standard procedure requires more than 24 hr, that still there are in many cases titration errors amounting to a few percent, and that his method is not suitable for the determination of small amounts of organic material because of the larger oxygen losses at lower permanganate concentrations.

Some years later, Stamm[31] made new progress in this field. He looked for a means to overcome the long reaction time of Imhof's procedure. He turned his attention to the fact that the reduction of permanganate to manganese dioxide in an alkaline solution takes place in two distinct steps, *viz.* the rapid reduction of permanganate to manganate and a much less rapid reduction of manganate to manganese dioxide. To limit the reaction time of oxidations by permanganate in an alkaline solution he

proposed the addition of so much permanganate to the organic material to be oxidised, that the reduction to manganate is sufficient for the desired oxidation. Indeed, Stamm succeeded by means of this idea to decrease the reaction time in some cases from several hr to several min, thus overcoming one of the major drawbacks of Imhof's procedures. To avoid oxygen losses Stamm carries out his analysis at large permanganate concentration (0·1*M*) and in as short a reaction time as possible. Although the reaction times are shorter in this case, still smaller permanganate concentrations have to be avoided because oxygen losses especially occur immediately after mixing permanganate and alkali (see Table IV and *Conclusions*).

Other valuable oxidimetric determinations of organic compounds by means of permanganate have been described since Stamm's work, but none of them has added new aspects to the solution of the problems mentioned above.

It may be concluded that sufficient experimental evidence is available to state that complicated oxidimetric determinations by means of permanganate taking much time should always be carried out at room temperature in solutions of which neither the acidity nor the alkalinity should be large (*e.g.* between 1*M* acid and 1*M* alkali). Titration errors caused by oxygen losses can never be corrected by running a blank, because an acidic blank loses only a little oxygen when no manganese^{II} or manganese dioxide (to catalyse the self-decomposition of permanganate in the determination itself) are present in the blank; an alkaline blank always develops more oxygen than the determination itself, because the stabilising manganate is formed, not only by the self-decomposition as in the blank, but also, and in many cases mainly, by means of reduction of permanganate by the compound to be determined.

Manganate. It has already been stated that the self-decomposition of permanganate in an alkaline solution does not pass beyond the manganate state. This means that manganate should be stable, with respect to loss of oxygen, in alkaline solutions. Although the normal potential of the manganate–manganese dioxide couple at pH 14 does not differ much from the permanganate–manganate and permanganate–manganese dioxide couples and manganate in this medium is, therefore, an oxidising reagent of the same strength as permanganate, Stamm's experimental work[31] demonstrates that permanganate is far more reactive than manganate. The smaller reactivity may, however, be compensated, or even over-compensated, by the greater stability resulting in the possibility of carrying out oxidations at higher temperatures without the loss of oxygen.

After preliminary work by den Boef,[26,32] in which the applicability of manganate for some quantitative inorganic oxidations and the stability at room temperature of manganate solutions were demonstrated, (results which were in accordance with results obtained by Issa *et al.*[33] somewhat later), Polak and den Boef[34] investigated the stability of manganate solutions at higher temperatures. Negligible loss of oxidative power was found when a 0·03*M* manganate solution was heated for 12 hr at 70° in 1 to 4*M* alkali hydroxide solution. Similar stability occurs on heating the same solutions at 100° for a few hr. Decreasing the manganate concentration to 0·006 *M* does not affect the stability under these conditions. This stability could be expected from the results of the decomposition of permanganate.[26]

It is of great practical importance that the presence of manganese dioxide does not affect the stability of manganate solutions. This means that when it is necessary to heat for a very long time so that some decomposition and loss of oxidative power

takes place, correction by means of a blank is possible, in contrast with analysis by means of permanganate. In alkali hydroxide solutions of concentration lower than 2*M* a slow disproportionation of manganate into permanganate and manganese dioxide takes place but this reaction does not, of course, bring about titration errors.

Polak[35] described a number of ways in which determinations with manganate can be carried out and applied them to the determination of formate ions, obtaining very accurate results with very small amounts of formate ions. A great number of other organic compounds can also be analysed with the same accuracy.[36]

Quadrivalent cerium

Cerium^{IV} compounds have been used extensively in oxidimetric processes since the work of Willard and Young,[37] although limited to strongly acidic solutions. The normal potential of the cerium^{IV}–cerium^{III} couple largely depends on the acidity and on the nature of the acid. It varies from 1·8 V in perchloric acid via 1·60 V in nitric acid and 1·45 V in sulphuric acid to 1·28 V in 1*M* hydrochloric acid. Thus cerium^{IV} is always a strong oxidising agent with an average of about the same strength as potassium permanganate. As a strong oxidant in an acidic medium it has, in general, surpassed its competitors for the following reasons:

(1) In a sulphuric acid medium (not in nitric or perchloric acids), solutions of cerium^{IV} sulphate can be boiled for several hr without any decomposition. This is a great advantage in slow oxidation processes, *e.g.* of organic compounds.
(2) The half reaction of the cerium^{IV}–cerium^{III} couple is a one electron transfer and therefore there are no unstable and highly reactive intermediates as is the case in the reduction of permanganate and dichromate in an acidic medium, so that induced reactions do not disturb the stoichiometry of an oxidation with cerium^{IV}.

There are also a few arguments against the use of cerium^{IV}:

(1) In spite of the high oxidation potential there is sometimes a lack of reactivity, so that catalysts are necessary to bring about the desired reaction, *e.g.* with arsenic^{III}.
(2) The limitation of its applicability to acidic solutions makes it unsuitable for the determination of compounds preferably or exclusively oxidised in neutral or alkaline solutions.

The latter limitation has been one of the main difficulties in the determination of organic compounds by complete oxidation with cerium^{IV}. Very often formic acid is one of the products of such oxidations and this compound is only incompletely oxidised by means of cerium^{IV} under normal conditions, so that correct results in the analysis of organic compounds could only be obtained by means of empirical factors.

Recently, Sharma and Mehrotra[38,39,40] indicated some new possibilities in solving this problem by means of the use of chromium^{III} as a suitable catalyst for the oxidation of some organic acids by means of cerium^{IV} to carbon dioxide and water in boiling 60% sulphuric acid. Without a catalyst Sharma[41] reported correct results for the oxidation of some carbohydrates to formic acid.

Very recently Mathur *et al.*[42] proposed potassium bromide as a catalyst in oxidations with cerium^{IV} of those organic compounds which normally yield formic acid without a catalyst. With bromide added, a few hr are sufficient for complete oxidation to carbon dioxide and water in 1*M* sulphuric acid.

In conclusion, the incomplete oxidation of organic compounds in an acidic medium is the main problem in the determination of organic compounds by complete

oxidative breakdown. As the work of the Indian investigators has already demonstrated, this problem has to be solved by means of the use of suitable catalysts.

Hexacyanoferrate (III)

The normal potential ($E_0 = 0{\cdot}356$ V) of the half reaction:

$$Fe(CN)_6^{3-} + e \rightleftarrows Fe(CN)_6^{4-}$$

is independent of the pH of the medium. Therefore, hexacyanoferrate (III) is a strong oxidising agent in alkaline solutions only. The reactivity is, however, not very large and the applications to organic analysis have been limited to some moderate oxidations, which have been reviewed recently.[9]

Potassium dichromate

The dichromate–chromium^{III} couple with a normal potential of 1·33 V at pH = 0 is only of interest in an acidic solution. In an alkaline solution dichromate is converted into chromate, which is not a strong oxidising agent.

For rapid oxidations dichromate has no advantage over permanganate and cerium^{IV}, but for slow processes it may be of interest because potassium dichromate is available in a very pure state, it does not decompose upon boiling in sulphuric acid solution and the difference between the normal potential of the cerium^{IV}–cerium^{III} couple and dichromate–chromium^{III} couple is too small to leave dichromate out of consideration for that reason alone. One must always, however, be prepared for induced side reactions.

Several quantitative determinations are known in which organic compounds, especially alcohols, are oxidised to carbon dioxide and water, but in many other processes the reaction is not stoichiometric.[43]

DISCUSSION

With this survey of the powerful oxidising agents in mind, some general rules of conduct for the complete oxidation of organic compounds will now be attempted, *i.e.* to see which oxidising agent should be selected and what should be the experimental conditions such as temperature and acidity.

Experimental results published by Pode and Waters[44] and by Imhof[30] and other data well known from organic chemistry give some knowledge about the pH at which organic compounds are preferably oxidised. Although there are exceptions, oxidations of some aliphatic acids *e.g.* malic acid, malonic acid, and nearly all aromatic acids, including phenolic compounds, proceed better in acidic than in alkaline media. On the contrary some other aliphatic acids, *e.g.* formic acid, lactic acid, alcohols, aldehydes and enolisable ketones can be better oxidised in an alkaline solution.

It is obvious that the oxidation of a complicated organic compound in a certain medium may result in products that are not further oxidised under the same conditions, so that for a further oxidation it will be necessary to change the conditions. For such a change, the pH of the solution must be particularly considered.

Imhof[30] has already described such a change in his standard procedure, consisting of a 24-hr oxidation of the organic compound in an alkaline medium with permanganate, followed by acidification of the reaction mixture and another 1 hr for further oxidation. This is a good procedure, for example, for oxidation of organic compounds that result in oxalic acid, which is not oxidised in an alkaline solution. The procedure should not, however, be generalised and in other cases the order

alkaline–acid might be better reversed *e.g.* in the oxidation of compounds being oxidised to formic acid in an acidic medium. The oxidation of formic acid is, as stated already, slow in an acidic medium and rapid in alkaline solution.

One can easily imagine that there could be oxidations in which a second change of medium would be useful to obtain a complete oxidation. Polak[36] demonstrated that the order alkaline oxidation–acid oxidation is in many cases not the best one and is in some cases without purpose, namely when no reaction occurs in an alkaline medium, *e.g.*, citric acid. He therefore critically examined every organic compound to be analysed before deciding to oxidise in either acid or alkaline solution only, or in both media. Thus, tartaric acid, fumaric acid and maleic acid are oxidised completely to carbon dioxide and water when the oxidation is started with acidic cold permanganate solution, continued in warm alkaline manganate solution and finished with a back titration in an acidic solution. On the other hand, pyruvic acid can be oxidised using in turn warm alkaline manganate–cold acid permanganate.

The data about the influence of the medium on the oxidation of organic compounds can also be applied to the analysis of mixtures. Some examples are:

(1) For a mixture of oxalic acid, formic acid and acetic acid,[34] the sum of oxalic acid and formic acid is determined by oxidation in an alkaline medium, then continued in an acidic medium; acetic acid remains unchanged. In an alkaline solution only formic acid is oxidised. The total acid can be obtained by means of an alkalimetric titration.

(2) For a mixture of formaldehyde and formic acid,[35] in an alkaline solution oxidation by manganate yields carbon dioxide and water. In the same medium formaldehyde can be determined by oxidation to formic acid according to Romijn.[6]
by manganate proceeds to carbon dioxide and water. In the same medium formaldehyde can be determined by means of oxidation to formic acid according to Romijn.[6]

(3) The same procedure can be applied to formaldehyde–methanol mixtures,[35] which are of practical importance.

When the influence of the medium on the oxidation of organic compounds is set aside and some attention given to the effect of temperature, it is obvious that the possibility of a high temperature is a great advantage.

In the survey of oxidising agents, it was seen that in an acidic medium only three of them had practical applications in the complete oxidation of organic compounds, namely permanganate, dichromate and cerium^{IV}, of which only the latter two can be used at boiling temperature in a sulphuric acid medium. In an alkaline solution only permanganate and manganate were of importance in the analysis under consideration, of which only the latter one could be used at higher temperatures.

When the influences of temperature and medium are combined it may be stated that permanganate is stable in an acidic and to a certain extent also in an alkaline medium, and that this is one of the reasons for its wide application in this field. However, the impossibility of working at higher temperatures requires further research in this field with other reagents *e.g.* by making use of an oxidation in two media of different acidity by means of two different reagents. An oxidation could be begun in a boiling sulphuric acid medium with cerium^{IV} or dichromate and continued in a warm alkaline solution with manganate or the reverse procedure. Better results appear possible by means of such procedures.

There is another section of this field in which attention has at present been revived, namely catalysis. To this process further attention should be given. It often opens up possibilities for new oxidations or it offers a more elegant procedure for an already known analysis. Very recently a number of investigations[19,42,45,46,47,58] using catalysts have been published.

Note. Apart from applications, already mentioned in this paper, the quantitative oxidation of an organic compound to carbon dioxide and water may be of value in its purity control. Very often the control of the purity of an organic acid is carried out by means of an alkalimetric determination. When, however, an acidic impurity is present false results are obtained. There is more certainty when a second procedure, *e.g.* an oxidimetric one, gives analogous results.

Zusammenfassung—Es wird eine Übersicht gegeben über die kräftige Oxidation organischer Substanzen in wässriger Lösung mittels sehr starker, zur quantitativen Analyse geeigneter, Oxydationsmittel. Deruss Einfl der Saüregrad der Lösung und die Möglichkeit bei höheren Temperaturen zu arbeiten werden besprochen.

Résumé—On présente une mise au point de l'oxidation forte en solutions aqueuses de corps organiques. Les influences de l'acidité des solutions et la possibilité de travailler à des températures elevées sont discutés.

REFERENCES

[1] W. M. Latimer, *Oxidation Potentials.* Prentice Hall Inc., 2nd Ed., 1952.
[2] D. M. West and D. A. Skoog, *Analyt Chem.*, 1959, **31,** 583.
[3] S. P. Rao, H. S. Rathi and J. N. Gaur, *Analyt. Chim. Acta,* 1961, **25,** 136.
[4] G. Gopalo Rao and B. V. S. R. Murty, *Z. analyt. Chem.*, 1960, **174,** 44.
[5] M. P. Fleury, *Chim. analyt.*, 1953, **35,** 197.
[6] G. Romijn, *Z. analyt. Chem.*, 1897, **36,** 18.
[7] I. M. Kolthoff and R. Belcher, *Volumetric Analysis, Volume III.* Interscience Publ. Inc., New York, 1957.
[8] C. L. Wilson and D. W. Wilson, *Comprehensive Analytical Chemistry, Volume IB.* Elsevier Publishing Company, 1960.
[9] B. R. Sant and S. B. Sant, *Talanta,* 1960, **3,** 261.
[10] E. Schulek, K. Burger and J. Laszlovsky, *ibid.*, 1960, **7,** 51.
[11] L. Erdey and I. Buzàs, *Acta Chim. Acad. Sci. Hung.*, 1955, **6,** 77.
[12] M. T. Berk, *ibid.*, 1955, **5,** 209.
[13] J. Minczewski and U. Glabisz, *Talanta,* 1960, **5,** 179.
[14] P. Pierron, *Bull. Soc. Chim.*, 1943, **10,** 445.
[15] J. Bitskei, *Acta Chim. Acad. Sci. Hung.*, 1956, **10,** 313.
[16] B. Singh and S. Singh, *Analyt. Chim. Acta,* 1958, **19,** 10.
[17] I. M. Kolthoff and V. A. Stenger, *Ind. Eng. Chem., Analyt.*, 1935, **7,** 79.
[18] H. A. Laitinen and D. E. Woerner, *Analyt. Chem.*, 1955, **27,** 215.
[19] F. Solymosi and J. Csik, *Chem. Analyst,* 1960, **49,** 12.
[20] S. Bose, *Analyt. Chem.*, 1958, **30,** 1526.
[21] I. M. Kolthoff, *Pharm. Weekblad,* 1924, **61,** 337.
[22] I. M. Kolthoff, *Die Massanalyse II.* Verlag Julius Springer, Berlin, 1928, 2e Auflage, p. 270.
[23] R. H. Ferguson, W. Lerch and J. E. Day, *J. Amer. Chem. Soc.*, 1931, **53,** 126.
[24] F. R. Duke, *ibid.*, 1948, **70,** 3975.
[25] M. C. R. Symons, *J. Chem. Soc.*, 1954, 3676.
[26] G. den Boef, *Z. analyt. Chem.*, 1959, **166,** 321.
[27] F. Marguérite, *Ann. Chim. Phys.*, 1846, **18,** 244.
[28] M. L. Péan de St. Gilles, *Ann. Chim. Phys.*, 1859, **55,** 374.
[29] W. Lenz, *Z. analyt. Chem.*, 1885, **24,** 34.
[30] J. G. Imhof, Dissertation, Utrecht, 1932.
[31] H. Stamm, *Die Reduktion von Permanganat zu Manganat als Grundlage eines neuen Titrationsverfahrens.* Akad. Verlag Halle, 1937.
[32] G. den Boef, J. den Boef-Nugteren and B. van Laar, *Z. analyt. Chem.*, 1959, **166,** 422.
[33] I. M. Issa, H. Khalifa and M. G. E. Allam, *ibid.*, 1960, **172,** 21.
[34] H. L. Polak and G. den Boef, *ibid.*, 1960, **175,** 265.
[35] H. L. Polak, *ibid.*, 1960, **176,** 34.
[36] *Idem, ibid.*, in press.

[37] H. Willard and P. Young, *J. Amer. Chem. Soc.*, 1928–1930, several papers.
[38] N. N. Sharma and R. C. Mehrotra, *Analyt. Chim. Acta*, 1954, **11**, 417.
[39] *Idem, ibid.*, 1954, **11**, 507.
[40] *Idem, ibid.*, 1955, **13**, 419.
[41] N. N. Sharma, *ibid.*, 1956, **14**, 423.
[42] N. K. Mathur, S. P. Rao and D. R. Chowdhary, *ibid.*, 1961, **24**, 533.
[43] L. J. Simon, *Compt. rend.*, 1920–1925, several papers.
[44] J. S. F. Pode and W. A. Waters, *J. Chem. Soc.*, 1956, 717.
[45] J. Sharp, *Analyt. Chim. Acta*, 1961, **25**, 139.
[46] W. H. McCurdy and G. Guilbault, *Analyt. Chem.*, 1960, **32**, 647.
[47] G. Guilbault and W. H. McCurdy, *ibid.*, 1961, **33**, 580.
[48] *Idem, Analyt. Chim. Acta*, 1961, **24**, 214.

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IMPROVED RADIOCHEMICAL DETERMINATION OF COBALT*

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Summary—A shortened procedure for the radiochemical determination of cobalt is described. The precipitation of cobalt mercury^{II} thiocyanate for the final yield determination, proposed by Hahn and Smith,[1] has been verified. Decontamination from 5-hr cooled fission products and 1-day cooled stainless steel activation products is complete.

RECENTLY Hahn and Smith[1] surveyed the then existing procedures for the radiochemical determination of cobalt. They concluded that the method of Burgus,[2] with a changed yield determination, was best. The change in yield determination was from the electrodeposition of cobalt to precipitation as cobalt mercury^{II} thiocyanate, $Co[Hg(SCN)_4]$.

At the time their article appeared, research in our laboratory had resulted in a method using this same precipitate. Our reasons for the selection of this precipitate are in complete agreement with those stated in the article. However, in our method the separation steps prior to the yield determination require only 45 min, resulting in a saving of over 1 hr in the overall procedure with no significant change in decontamination. Omitting the potassium cobaltinitrite and sulphide precipitations, two of the more tedious steps, accounts for most of the time saving.

EXPERIMENTAL

Procedure

1. Place an aliquot of sample in a 50-ml centrifuge containing 1 ml of cobalt carrier [10 mg/ml as $Co(NO_3)_2$]. Add sufficient sodium hydroxide to precipitate $Co(OH)_2$ completely. Centrifuge and discard the supernatant solution.
2. Dissolve the precipitate in a minimum (*ca.* 2 drops) of conc. sulphuric acid. Heat, if necessary, until dissolution is complete and the cobalt red colour appears. Cool, add 2 ml of conc. ammonium hydroxide solution, and dilute to 10 ml with water.
3. Slowly add 10 drops of 10 mg/ml iron^{III} holdback while vigorously swirling the solution. Centrifuge and decant (or filter) into a 125-ml separatory funnel.
4. Add 2 ml of glacial acetic acid, 20 ml of 25% ammonium thiocyanate solution (pH 7·0), and 10 ml of methyl isobutyl ketone. Extract for 1 min. Discard the aqueous phase.
5. Add 20 ml of 25% ammonium thiocyanate solution and scrub the organic phase for 1 min. Discard the aqueous phase. Repeat.
6. Strip the cobalt with 5 ml of water for 30 sec. Drain the aqueous phase into a clean 50-ml centrifuge tube. Repeat the strip with an additional 5 ml of water, combining the aqueous portions. Add 3 drops of conc. hydrochloric acid.
7. Heat nearly to boiling and add 2 ml of 1*M* ammonium mercury^{II} thiocyanate. Swirl until precipitation of the blue cobalt thiocyanate is complete, as evidenced by the lack of red colour in solution.
8. Cool in an ice bath and filter onto a tared filter. Wash with water, ethanol, and ether. Dry for 5 min in a vacuum desiccator and weigh as $Co[Hg(SCN)_4]$ (11·98% by weight cobalt).

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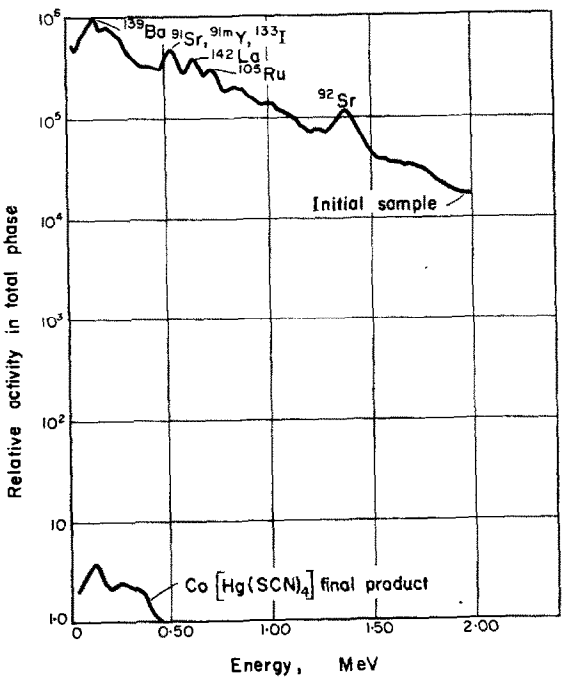


FIG. 1.—Decontamination from 5-hr cooled fission products.

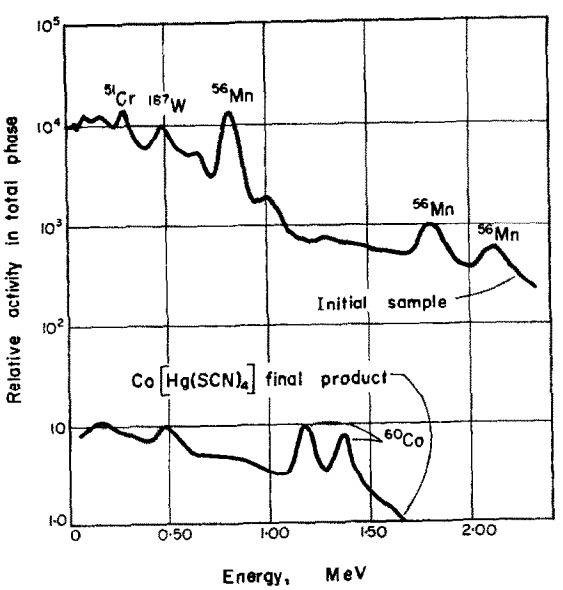


FIG. 2.—Decontamination from 1-day cooled stainless steel activation products.

The gamma ray spectra shown in Figs. 1 and 2 illustrate the decontamination of cobalt from 5-hr cooled fission products and 1-day cooled stainless steel (Bureau of Standards Sample No. 123-A) activation products.

Zusammenfassung—Es wird ein gekurztes Verfahren zur radiochemischen Bestimmung von Kobalt beschrieben. Die Fällung von Kobalt mercurirhodanid wird nach Hahn und Smith für die endliche Bestimmung bestätigt. Die Entgiftung ist aus 5-Stunde-gekühlt Spaltprodukten und 1-Tag-gekühlt-Nichtröstende-stahl-Aktivierungsprodukten völlig.

Résumé—Les auteurs décrivent une méthode simplifiés de dosage radiochimique du cobalt. La précipitation du mercurithiocyanate de cobalt pour le dosage final, proposée par Hahn et Smith, a été vérifiée. La décontamination des produits de fissions refroidis pendant 5 heures et des produits d'activation de l'acier inoxydable refroidis pendant 1 jour est complète.

REFERENCES

[1] R. B. Hahn and D. L. Smith, *Talanta*, 1961, **7**, 291.
[2] W. H. Burgus, *Collected Radiochemical Procedures*, edited by J. Kleinberg. Atomic Energy Comm. Rept. LA-1721 (Rev.), November 18, 1955, pp. 66–72.

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TITRIMETRIC DETERMINATION OF VANADIUM^{IV} WITH CERIUM^{IV} SULPHATE AT ROOM TEMPERATURE USING RHODAMINE 6G AS FLUORESCENT INDICATOR

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Summary—The titration of vanadium^{IV} has been carried out with cerium^{IV} sulphate at room temperature in a medium containing sulphuric acid and syrupy phosphoric acid, using Rhodamine 6G as an internal fluorescent indicator. At the equivalence point the greenish-yellow fluorescence of the indicator is suddenly quenched with a slight excess of the oxidant.

FROM a potentiometric study of the titration of vanadium^{IV} with cerium^{IV} sulphate, Furman[1] found that accurate results are obtained at room temperature only when the titration is carried out slowly in the neighbourhood of the end-point and waiting for several min for the potential to become constant. Furman reported that the titration can be carried out at 50–60° as the rate of reaction is rapid at this temperature, and that the titration is as satisfactory as the permanganate titration is at 80°. According to Furman the break in potential at the end-point per 0·05 ml of 0·05*N* cerium^{IV} solution varies from 25 to 100 mV as the initial volume of the solution is varied between 200 and 25 ml, respectively. Willard and Young[2] independently studied the same titration and found that titrations at 70–80°, using 5–15 ml of sulphuric acid per 100 ml of the titration mixture, give accurate results when carried out in either direction, although the break in potential at the end-point decreases as the acidity is increased.

Kolthoff and Belcher[3] state that no visual end-point methods appear to have been described for the determination of vanadium^{IV}. Willard and Young[4] appear to have investigated without success the use of ferroïn as an internal indicator in this titration.

From the experiments of Furman (*loc. cit.*) and Willard and Young (*loc. cit.*) it appears that the reaction between vanadium^{IV} and cerium^{IV} sulphates is slow at room temperature. During a study of the possible influence of various catalysts, we observed that orthophosphoric acid (overall concentration 0·30–0·45*M*) markedly accelerates the reaction in dilute sulphuric acid, so that the titration of vanadium^{IV} with cerium^{IV} sulphate can then be made at room temperature using Rhodamine 6*G* as a fluorescent indicator. The equivalence point is indicated by a sudden quenching of the fluoresence of Rhodamine 6G with the addition of a very slight excess of cerium^{IV} sulphate solution. Without the presence of the phosphoric acid catalyst, Rhodamine 6G gives a correct indication of the end-point when the titration is carried out at 70–80°.

EXPERIMENTAL

Reagents

Vanadium^{IV} Sulphate Solution, approximately 0·05*N*: Prepared by reducing an aliquot volume of about 0·1*N* sodium vanadate solution in a sulphuric acid medium with sulphur dioxide at boiling temperature, then making up the solution to the desired volume after having driven off the sulphur dioxide completely by passing a rapid stream of carbon dioxide.

Cerium sulphate solution approximately 0·05*N*: Prepared in the usual manner from B.P. cerium oxalate free from iron, and standardised against B.D.H. AnalaR quality sodium oxalate.

Orthophosphoric acid: Syrupy phosphoric acid of Pro Analysi grade supplied by E. Merck (Germany).

0·035% *Rhodamine 6G solution:* Prepared from Rhodamine 6G supplied by B.D.H. Ltd. and stored in an amber coloured bottle.

All other chemicals used in this investigation were of analytical reagent grade.

Catalytic effect of orthophosphoric acid

The following experiments were made to demonstrate the accelerating action of orthophosphoric acid on the reaction between vanadium^{IV} and cerium^{IV} sulphates: 0·5 ml of approximately 0·01*N* vanadium^{IV} sulphate solution was added to 50 ml of 2·0*N* sulphuric acid. To this mixture was added 0·2 ml of 0·035% Rhodamine 6G solution. The resulting mixture had a greenish-yellow fluorescence in the diffuse light of the laboratory. Such a mixture was treated with varying volumes of approximately 0·01*N* cerium^{IV} sulphate solution, while being stirred with a magnetic stirrer, and the observations are recorded in Table I. Similar experiments were also made in the presence of 1·0 ml of syrupy phosphoric acid.

In the above experiments, the concentration of vanadium^{IV} was equivalent to what obtains

TABLE I

Serial no.	Volume of cerium^{IV} sulphate solution added, *ml*	Observations	
		A—In absence of phosphoric acid	B—In presence of 1·0 ml of syrupy phosphoric acid
1	0·10	Intensity of fluorescence decreases somewhat; original intensity restored after 20 sec.	No change in intensity of fluorescence
2	0·20	Fluorescence nearly completely quenched, but begins to reappear in 20 sec, reaching original intensity in about 40 sec.	No change in intensity of fluorescence.
3	0·30	Fluorescence completely quenched, but begins to reappear after 25 sec; maximum intensity is reached in 60 sec, but original intensity not regained.	Intensity of fluorescence decreases somewhat, but regains original intensity almost immediately.
4	0·40	Fluorescence completely quenched; feeble fluorescence reappears after 45 sec and intensifies with time; original intensity not regained.	Intensity of fluorescence decreases somewhat, but begins to intensify almost immediately, reaching original intensity in 5 sec.
5	0·50	Fluorescence completely quenched; fluorescence begins to appear in 85 sec and intensifies in 120 sec; original intensity not regained.	Fluorescence completely quenched, but almost immediately reappears, reaching original intensity in about 10 sec.
6	0·55	Fluorescence completely quenched; very feeble fluorescence reappears after 150 sec but does not intensify with time.	Fluorescence completely quenched, but reappears after 5 sec; intensity low and does not increase with time.
7	0·60	Fluorescence immediately quenched, and does not reappear even after 5 min.	Fluorescence immediately quenched and does not reappear even after 5 min.

towards the equivalence point of a titration of 0·05*N* solution. The amount of vanadium^{IV} taken was equivalent to 0·51 ml of the cerium^{IV} sulphate solution used in these experiments.

Rhodamine 6G appears to undergo ready oxidation by cerium^{IV} sulphate to an intermediate oxidation product, which may be in the nature of a free radical and is practically non-fluorescent. The intermediate oxidation product can undergo reduction by vanadium^{IV} sulphate somewhat slowly, or undergo further oxidation by cerium^{IV} sulphate to an irreversible state which is also non-fluorescent. In experiments 2A and 3A it is seen that the fluorescence is almost completely quenched, immediately on the addition of cerium^{IV} sulphate, although there is vanadium^{IV} sulphate present in excess of the amount of cerium^{IV} sulphate added. From this observation, it is concluded that the reaction between Rhodamine 6G and cerium^{IV} sulphate is much more rapid than the vanadium^{IV}–cerium^{IV} sulphate reaction. Consequently, the cerium^{IV} sulphate added reacts with Rhodamine 6G in preference to vanadium^{IV}. In the corresponding experiments 2B and 3B, where phosphoric acid is present, it is observed that the fluorescence is practically unaffected. This observation leads to two conclusions:[1] that cerium^{IV} sulphate reacts rapidly with vanadium^{IV} in the presence of phosphoric acid, and[2] that any oxidised Rhodamine 6G is rapidly reduced back to the original fluorescent form by vanadium^{IV}, this reduction being more rapid in the presence of phosphoric acid than in its absence. These conclusions receive further support from experiments 5A and 5B. In experiment 5A, the amount of cerium^{IV} sulphate added is nearly equivalent to the vanadium^{IV} present, but the fluorescence of Rhodamine 6G is completely quenched, a feeble fluorescence reappearing only after 85 sec. This shows that in the absence of phosphoric acid: (1) Rhodamine 6G is oxidised in preference to vanadium^{IV}, and (2) reduction of the intermediate oxidised product of Rhodamine 6G by vanadium^{IV} is so slow that it is further oxidised by cerium^{IV} to the irreversible product. However, in the corresponding experiment 5B where phosphoric acid is present, it is noted that although the fluorescence of the dye is quenched immediately on the addition of cerium^{IV}, it reappears almost immediately, reaching the original intensity in about 10 sec. This result indicates that: (1) the vanadium^{IV}–cerium^{IV} reaction is accelerated by phosphoric acid, and (2) although Rhodamine 6G is oxidised to the intermediate state, it is very quickly reduced back to the fluorescent dye because of the acceleration by phosphoric acid. In experiment 7B, the fluorescence is completely quenched although there is phosphoric acid present. This is so because the cerium^{IV} sulphate added is in excess of that required for the complete oxidation of the vanadium^{IV} present. The amount of Rhodamine 6G added to the solution requires about 0·08 ml of 0·01*N* cerium^{IV} sulphate for complete oxidation.

Experiments similar to those recorded in Table I have been conducted with more concentrated solutions of vanadium^{IV} and cerium^{IV} and the observations recorded in Table II.

The observations recorded in Table II lead to the same conclusions as those in Table I. In experiments 1B, and 2B, there is no quenching of the fluorescence whereas in experiments 3B, 4B and 5B, even though the fluorescence is quenched, it is very rapidly regained. Evidently phosphoric acid present in the mixture accelerates the reaction between vanadium^{IV} and cerium^{IV} so much that there is no cerium^{IV} left for the oxidation of Rhodamine 6G; or even if the dye is oxidised, it is only to the intermediate free radical state, which is again rapidly reduced back to the fluorescent dye by the vanadium^{IV} present, because this reaction is also accelerated by phosphoric acid. In experiment 6B, the cerium^{IV} salt added is slightly in excess of the vanadium^{IV} present, so that the dye is oxidised to the irreversible non-fluorescent state.

In view of the above findings, it may be concluded that the titrimetric determination of vanadium^{IV} is possible at room temperature using orthophosphoric acid as catalyst and Rhodamine 6G as internal indicator.

Factors influencing the oxidation of Rhodamine 6G by cerium^{IV}

In order to ascertain the optimum conditions for the best functioning of the indicator, the following experiments were made on the speed of the reaction between cerium^{IV} sulphate and Rhodamine 6G at various acidities in the presence and absence of phosphoric acid, cerium^{III} sulphate and vanadium^{IV}. The observations are recorded in Table III.

The observations in Table III show that the oxidation of Rhodamine 6G by cerium^{IV} sulphate is retarded by phosphoric acid but the retardation decreases as the acid concentration is increased. When the concentration of sulphuric acid is 2·0*N*, the oxidation of the dye is immediate even in the presence of 2·0 ml of syrupy phosphoric acid.

Because phosphoric acid is necessary for the acceleration of the reaction between vanadium^{IV} and cerium^{IV}, it is seen that for a satisfactory titration of vanadium^{IV} with cerium^{IV} using Rhodamine 6G as internal indicator, the acidity should be between 1·5 and 2·0*N*. In these limits of sulphuric acid concentration, 1·0 to 1·5 ml of syrupy phosphoric acid is sufficient to accelerate the reaction between vanadium^{IV} and cerium^{IV}; the acidity is sufficient to counteract the retarding influence of phosphoric acid on the oxidation of the dye by cerium^{IV}. However, the acidity cannot be made too high, because vanadium^{V} itself is capable of oxidising the dye in 4·0*N* sulphuric acid or in 3·0*N* sulphuric acid in the

presence of phosphoric acid, as shown in the last two experiments of Table III. The addition of cerium^{III} sulphate has been observed to have no effect on the speed of oxidation of the dye.

Factors influencing the reduction of Rhodamine 6G by vanadium^{IV}

It has already been stated that the immediate quenching of the fluorescence of Rhodamine 6G by cerium^{IV} appears to be caused by the oxidation of the dye to an intermediate free radical state, which is non-fluorescent and that the dye in the free radical state can be reduced back to the original

TABLE II

Serial no.	Volume of cerium^{IV} sulphate solution added, *ml*	Observations	
		A—In absence of phosphoric acid	B—In presence of syrupy phosphoric acid
1	0·10	Fluorescence disappears but begins to reappear after 4 sec and reaches maximum intensity in 10–15 sec.	No change in the intensity of fluorescence.
2	0·20	Fluorescence completely quenched but begins to reappear after 8 sec, reaching maximum intensity in 20 sec.	Intensity of fluorescence decreased somewhat but almost immediately regains original intensity.
3	0·30	Fluorescence completely quenched; begins to reappear after 13 sec, reaching maximum intensity after 30 sec.	Fluorescence quenched but almost immediately reappears, regaining original intensity in 5 sec.
4	0·40	Fluorescence completely quenched but begins to reappear after 25 sec, reaching maximum intensity after 50 sec but much lower than original intensity.	Fluorescence completely quenched but begins to reappear in 2 sec, and intensifies in 10 sec.
5	0·45	Fluorescence completely quenched but begins to reappear after 60 sec; intensity of fluorescence very feeble even after long time.	Fluorescence completely quenched but begins to reappear in 3 sec, regaining original intensity in 10 sec.
6	0·51	Fluorescence completely quenched, and does not reappear even after 5 min.	Fluorescence completely quenched, and does not reappear even after 5 min.

50 ml of 2·0*N* sulphuric acid +0·5 ml of vanadium^{IV} solution (0·05443*N*) + 0·2 ml of 0·035% Rhodamine 6G solution. Concentration of cerium^{IV} sulphate solution = 0·05539*N*.

fluorescent dye by vanadium^{IV} or other suitable reductant. Unless the speed of this reduction is rapid, the indicator cannot function properly. If the indicator is oxidised rapidly by cerium^{IV} to the intermediate oxidation product (or even to the final irreversible product) and if the speed of reduction of the intermediate product by vanadium^{IV} is not very fast, it is obvious that premature end-points will result. Hence experiments were made to ascertain the factors which control the reduction of the partially oxidised dye by vanadium^{IV} in the following way: To 50 ml of dilute sulphuric acid, 0·2 ml of 0·035% Rhodamine 6G solution was added, followed by 0·5 ml of 0·005*N* cerium^{IV} sulphate solution, then 0·5 ml of 0·005*N* vanadium^{IV} sulphate solution. If the influence of phosphoric acid was to be studied, it was added before the vanadium^{IV}. Observations were made concerning the times of first appearance of fluorescence of the dye and these are recorded in Table IV. The fluorescence intensifies gradually after the time indicated.

In the experiments marked by an asterisk, the fluorescence is restored by the mere addition of phosphoric acid, without the addition of any vanadium^{IV}. This is probably caused by the acceleration of the disproportionation of the partially oxidised dye by phosphoric acid, The accelerated disproportionation is observed only in media containing sulphuric acid of a concentration not exceeding 1·0*N*.

At higher acid concentrations, the fluorescence is restored only on adding vanadium^{IV}. From the results in Table IV, it is seen that: (1) the reduction of the partially oxidised dye by vanadium^{IV} is a somewhat slow reaction, (2) the speed of reduction is decreased by increasing the concentration of sulphuric acid, and (3) the speed of reduction of the partially oxidised dye by vanadium^{IV} is accelerated by phosphoric acid. A volume of 0·5–1·0 ml of syrupy phosphoric acid is sufficient to accelerate

TABLE III

Additives	Time of quenching of fluorescence of Rhodamine 6G, *sec*						
	0·2*N* H_2SO_4	0·5*N* H_2SO_4	1·0*N* H_2SO_4	1·5*N* H_2SO_4	2·0*N* H_2SO_4	3·0*N* H_2SO_4	4·0*N* H_2SO_4
0·05 ml of 0·05*N* Ce^{IV}	immediate	immediate	immediate	immediate	immediate	immediate	immediate
0·05 ml of 0·05*N* Ce^{IV} + 0·50 ml of syrupy phosphoric acid	135	40	2	immediate	immediate	immediate	immediate
0·05 ml of 0·05*N* Ce^{IV} + 1·0 ml of syrupy phosphoric acid	180	80	5	immediate	immediate	immediate	immediate
0·05 ml of 0·05*N* Ce^{IV} + 2·0 ml of syrupy phosphoric acid	480	130	20	2	immediate	immediate	immediate
5·0 ml of 0·1*N* of sodium vanadate	—	—	—	—	—	—	30
5·0 ml of 0·1*N* sodium vanadate + 1·0 ml of syrupy phosphoric acid	—	—	—	—	—	15	5

Total volume of the reaction mixture 50 ml + 0·2 ml of 0·035% Rhodamine 6G solution.

TABLE IV

Volume of syrupy phosphoric acid added, *ml*	Time of restoration of fluorescence, *sec*						
	0·2*N* H_2SO_4	0·5*N* H_2SO_4	1·0*N* H_2SO_4	1·5*N* H_2SO_4	2·0*N* H_2SO_4	3·0*N* H_2SO_4	4·0*N* H_2SO_4
nil	7	10	12	15	20	30	35
0·5	*	*	*	immediate	immediate	10	12
1·0	*	*	*	immediate	immediate	8	10
2·0	*	*	*	immediate	immediate	5	8

the speed of reduction in a 1·5–2·0*N* sulphuric acid medium. Moreover, it has also been observed that, in the presence of phosphoric acid, the fluorescence restored by vanadium^{IV} intensifies much more quickly than in the absence of phosphoric acid.

Recommended procedure for the titrimetric determination of vanadium^{IV} using Rhodamine 6G as indicator and phosphoric acid as catalyst

From 5 to 20 ml of 0·05*N* vanadium^{IV} solution are transferred to an Erlenmeyer flask and sufficient dilute sulphuric acid is added to give an overall acidity of 1·5–2·5*N* when diluted to 50 ml. The mixture is then treated with 1·0–1·5 ml of syrupy phosphoric acid and 0·2 ml of 0·035% Rhodamine 6G solution and titrated at room temperature with a standard solution of 0·05*N* cerium^{IV} sulphate, containing sulphuric acid at about 1·0*N*. The titration is carried out with the usual speed until the greenish-yellow fluorescence of the mixture is quenched. Towards the end of the titration,

it is better to add the cerium^{IV} sulphate in fractions of a drop to avoid any indicator correction when working with 0·05*N* solutions of vanadium^{IV} and cerium^{IV}. Titrations can be made normally in a well-lighted laboratory, without the need for an artificial source of illumination; on a cloudy day, however, titrations should be made with the use of a 100 W incandescent lamp. It should be noted that the light transmitted by Rhodamine 6G is red, whereas the fluorescence light is greenish-yellow. Observations of the change in intensity of the fluorescent light are facilitated by holding a piece of black paper behind the titration flask. When phosphoric acid is used as a catalyst, titrations cannot be made in 0·5–1·0*N* sulphuric acid media, because of the possibility of the precipitation of cerium^{IV} phosphate and of the retardation of the oxidation of the indicator.

Some typical results from a large number of determinations of vanadium^{IV} are presented in Table V. Titrations of 0·01*N* solutions of vanadium^{IV} are also possible under the conditions described above. An indicator correction of 0·08 ml of 0·01*N* cerium^{IV} sulphate solution should be applied.

TABLE V

Titration with 0·05*N* vanadium^{IV} solution		Titration with 0·01*N* vanadium^{IV} solution	
Vanadium^{IV} taken, *mmole*	Vanadium^{IV} found, *mmole*	Vanadium^{IV} taken, *mmole*	Vanadium^{IV} found, *mmole*
0·2674	0·2681	0·02927	0·02908
0·3553	0·3538	0·04060	0·04080
0·4454	0·4448	0·05286	0·05277
0·5554	0·5554	0·06042	0·06033
0·6368	0·6401	0·06609	0·06591
0·8600	0·8568	0·07647	0·07656
1·0070	1·0020		
1·0230	1·0200		

Titration of vanadium^{IV} with cerium^{IV} sulphate at 70–80°

Titrations of vanadium^{IV} can be carried out with cerium^{IV} sulphate in a 0·5–2·5*N* sulphuric acid medium at 70–80°, using 0·2 ml of 0·035% Rhodamine 6G solution as indicator. At this high temperature, there is no need for the use of phosphoric acid as a catalyst, because both reactions—the oxidation of vanadium^{IV} by cerium^{IV} sulphate and the reduction of the semi-oxidised indicator by vanadium^{IV}—are very fast. There is no need to use an inert atmosphere. Titrations are not possible in media containing sulphuric acid at 3·0*N* and above, because higher acid concentrations tend to destroy the fluorescence of Rhodamine 6G. Some typical results are given in Table VI.

TABLE VI

Amount of vanadium	
Taken, *mmole*	Found, *mmole*
0·2402	0·2412
0·2952	0·2947
0·3128	0·3121
0·4303	0·4204
0·6005	0·5985

Titrations in hydrochloric acid media

Titrations of vanadium^{IV} in hydrochloric acid media using phosphoric acid as catalyst and Rhodamine 6G as indicator have been found to be possible only when the hydrochloric acid concentration is about 2·5–3·5*N*. Below 2·5*N* acid concentration, there is some slight precipitation of cerium^{IV} phosphate and above 3·5*N* hydrochloric acid concentration, the fluorescence of Rhodamine 6G decreases because of the acid itself. Without the use of phosphoric acid, titrations of vanadium^{IV} are possible at 80° in a 0·5*N* hydrochloric acid medium, using the Rhodamine 6G indicator. When the acid concentration is higher, the fluorescence of Rhodamine 6G is decreased because of the combined effect of the increased acid concentration and higher temperature.

Interferences

Iron^{III} and chromium^{III}: The results in Table VII show that iron^{III} does not interfere in the cerimetric determination of vanadium^{IV} using Rhodamine 6G as indicator and phosphoric acid as catalyst at room temperature. With chromium^{III} there is no interference up to about 5 ml of 0·05*M* chromium^{III} sulphate in 50 ml of the titration mixture, but above this concentration it is difficult to note the fluorescence of Rhodamine 6G. It will also be seen from the results in Table VII that iron^{III} and chromium^{III} do not interfere even when present together at the maximum limits.

TABLE VII

Additive, *ml* 0·05*M solution*	Vanadium^{IV} found, *mmole*
2·0 of iron^{III}	0·2859
3·0 of iron^{III}	0·2859
5·0 of iron^{III}	0·2880
10·0 of iron^{III}	0·2869
2·0 of chromium^{III}	0·2880
3·0 of chromium^{III}	0·2859
5·0 of chromium^{III}	0·2880
2·0 ml of iron^{III} + 3·0 ml of chromium^{III}	0·2869

Amount of vanadium^{IV} taken = 0·2869 mmole.

Uranium^{IV}, molybdenum^{V} and iron^{II}: Uranium^{IV}, molybdenum^{V} and iron^{II} also react quantitatively with cerium^{IV} sulphate under the conditions prescribed for the titration of vanadium^{IV} in the presence of phosphoric acid at room temperature, using the Rhodamine 6G indicator.

Use of other catalysts

Osmium^{VIII}, iron^{III}, chromium^{III}, and manganese^{II} do not accelerate the reaction between vanadium^{IV} and cerium^{IV} sulphate in 1·0*N* sulphuric acid.

Zusammenfassung—Die Titration von Vanadin(IV) mit Cer(IV) sulfate bei Raumtemperatur wurde mit Rhodamin 6G als Fluorescenzindicator durchgeführt. Das Titrationsmedium enthielt konzentr. Schwefelsäure und syrupöse Phosphorsäure. Beim Äquivalenzpunkt wird die gelbgrüne Fluoreszenz des Indicators abrupt gelöscht, wenn ein kleiner Überschuss von Oxyadtionsmittel anwesend ist.

Résumé—Les auteurs ont effectué le titrage du vanadium(IV) par le sulfate de cérium(IV) à température ambiante dans un milieu contetant de l'acide sulfurique et de l'acide phosphorique concentré; la rhodamine 6G est utilisée comme indicateur fluorescent interne. Au point équivalent, la fluorescence jaune grisâtre de l'indicateur disparaît brusquement pour un faible excès d'oxydant.

REFERENCES

[1] N. H. Furman, *J. Amer. Chem. Soc.*, 1928, **50**, 1675.
[2] H. H. Willard and P. Young, *Ind. Eng. Chem., Analyt.*, 1928, **20**, 972.
[3] I. M. Kolthoff and R. Belcher, *Volumetric Analysis*, Vol. III. Interscience Publishers Inc., New York, 1957, p. 146.
[4] H. H. Willard and P. Young, *J. Amer. Chem. Soc.*, 1933, **55**, 3267.

Talanta, 1962, Vol. 9, pp. 297 to 323. Pergamon Press Ltd. Printed in Northern Ireland

ANALYTICAL POTENTIAL OF SEPARATIONS BY LIQUID ION EXCHANGE

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Summary—While extractions by liquid anion exchange with alkylamines or quaternary ammoniums and by liquid cation exchange with (especially) organophosphorus acids are being developed intensively for chemical processing, they appear as yet to be used considerably less than other types of extractions in analytical chemistry. It is suggested that this results from chance and habit rather than from any lack of potential usefulness, and that liquid ion exchange warrants increased attention from analytical chemists. Some of the advantages that have proved important in chemical processing should apply also to analytical use. When extractions reported from process and physicochemical applications are included along with analytical reports, a considerable range of extractions is already available to suggest and guide further uses. A representative compilation of such extractions is summarised, and the controlling variables in some of the typical liquid ion-exchange systems are reviewed.

FOR the purpose of this paper, *liquid ion exchange* refers to those liquid-liquid extraction systems that operate, at least formally, by interchange of ions at the interface between an aqueous solution and an immiscible solvent, with negligible distribution of the extracting agent to the aqueous phase. Neither of these criteria is precise. *Negligible* is an elastic description, and some of the extraction systems (as also some resinous ion-exchange systems) can involve transfer of a neutral species followed by further complexing within the organic phase instead of actual interchange of ions. However, those equilibria can still be validly represented as the equivalent exchange of complex ion for free ligand ion, and the definition is useful to distinguish extractions by ionic systems from extractions by chelation systems, by neutral reagents like ethers, esters, and phosphine oxides, and by distribution of complex species already formed in the aqueous phase.

While the preference emphasised for extraction reagents showing only negligible transfer to the aqueous phase is not as essential to analytical extractions as it is to process extractions, it still has advantages to offer. These include avoiding the loss of extraction power by loss of reagent or by competition from that portion of the reagent transferred to the aqueous phase, reproducibility over changing extraction conditions, constant reagent concentration through multistage extractions, and constant composition for final colorimetric determinations in the organic phase.

In comparison with the recent rapid expansion of analytical use of other extraction systems, liquid ion exchange has not yet been much exploited. In a review by Morrison and Freiser in 1960,[75] only 4 of about 150 analytical extractions tabulated are of this type, and none in their review in 1958.[74] Instead of accepting that as evidence of low potentiality, it is a purpose of this paper to suggest that liquid ion exchange warrants increased attention, and to summarise a range of liquid ion exchange extractions from process and physicochemical as well as analytical studies

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to help provide a basis for their increased application. (*Cf.* reference 71, a recent monograph on amine extraction.)

Nearly all anion-exchange extractions have used alkylamines or quaternary ammoniums, and most of the cation-exchange extractions have used organophosphorus acids. Previous publications[13,32] have summarised the backgrounds of each, starting in 1948 with alkylamines[94] and in 1949 with butyl phosphoric acids.[47,73,95] Other cation-exchange systems include carboxylic acids,[48] fluorocarboxylic acids,[63] and sulphonic acids.[17] Cation-exchange extractions are arranged in Table I and anion-exchange extractions in Table II under element, valency, major component of aqueous phase, type or class and name of extracting reagent, and diluent. These listings are intended to be representative rather than exhaustive, because many duplications and parallels to some of the extractions could have been cited from

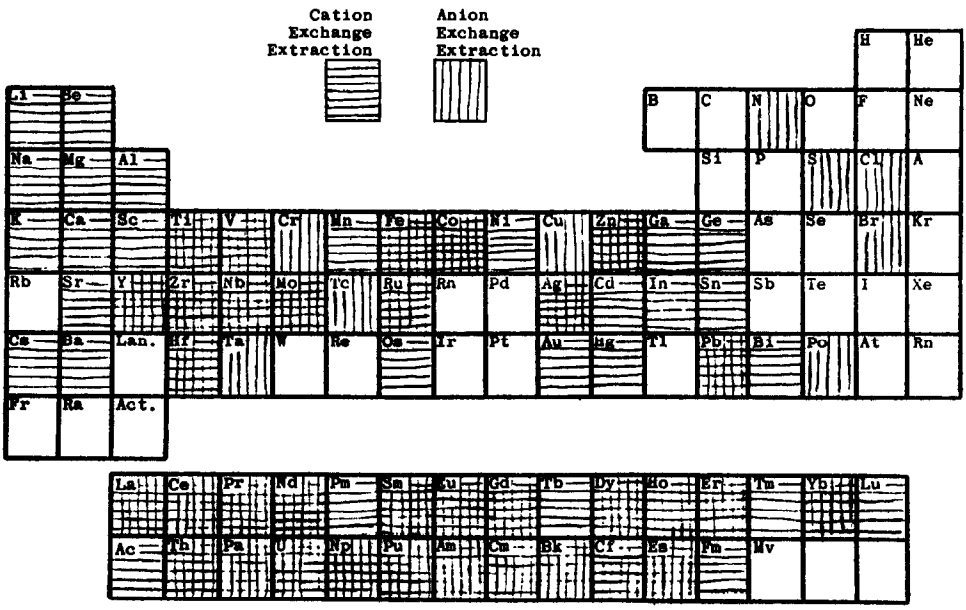


FIG. 1—Summary of elements reported to be extracted by liquid cation and anion exchange.

different sources. Many of the sources cited describe or at least indicate further extraction systems, and some provide extensive reference lists. It should be noted that the present listings do not purport to reflect credits for priority in the development of either general or specific systems.

Many of the reagents are listed by abbreviation, commercial designation, or incomplete chemical name. These are identified more fully in Table III, which also lists sources (preferably commercial) when known. Frequently there are more commercial sources than listed. On the other hand, some reagents may not now be available from the sources cited, because they may have been furnished from limited stocks of research samples.

Some general trends noted in the tables are illustrated in the small periodic charts. Fig. 1 summarises the elements reported extracted, comparing cation and anion

exchange. Only the cation exchange extends into the alkaline earth and alkali elements. Anion exchange extends further into the metalloids and, of course, includes the hydro- and oxygen acids. Both have been used extensively for the transition metals. It is also noticeable that there has been much attention devoted to the actinides and lanthanides. This reflects the intensive study of these extractions in reactor fuels, raw materials and reprocessing. A blank does not necessarily indicate non-extractability—it may be only lack of information. For instance, the lanthanides missing for some of the extractant classes (Figs. 2–4) certainly must behave somewhat like their neighbours, but they are the rarer ones and were not actually analysed in the studies cited.

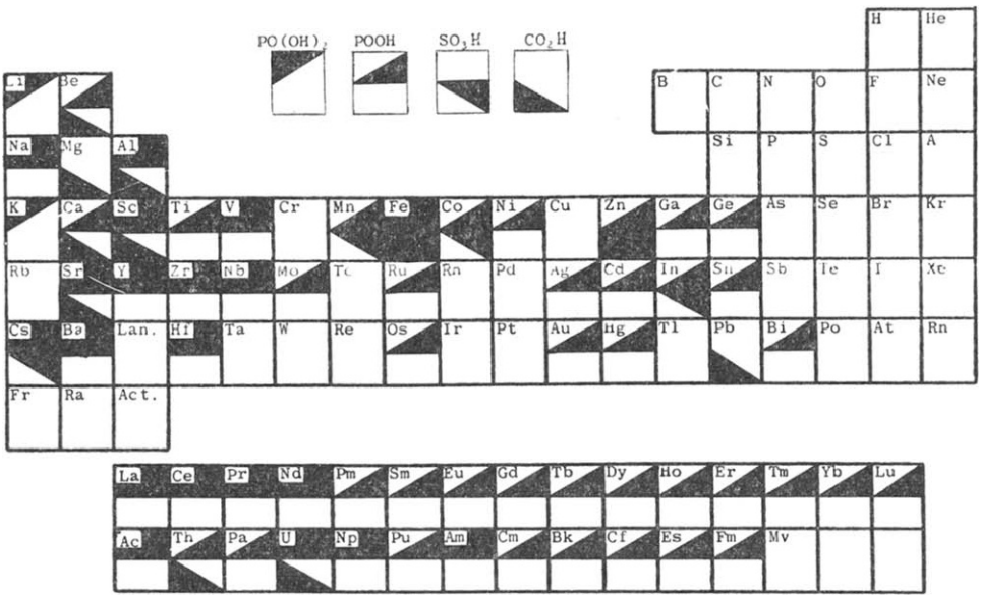


FIG. 2—Extractions with acids.

The reagents and conditions of these extractions are sorted out a step further in Figs. 2–4. Fig. 2 shows the cation-exchange extractions, comparing the use of (1) dibasic monoalkylphosphoric and -phosphonic acids, (2) monobasic dialkylphosphoric and -phosphinic acids, (3) sulphonic acids, and (4) carboxylic acids. Dialkylphosphoric acids have the major share of these reported extractions. Sulphonic and carboxylic acids have as yet been tested to only a slight extent, but probably have an important future.

Fig. 3 shows the extractions with primary amines from solutions in which the major anion was nitrate, chloride, sulphate, or phosphate. The nature of the aqueous anions is more significant here than in cation exchange, where they only exert varying degrees of competition with the reactant, since in anion exchange they often must contribute to forming the extractible species. It is characteristic that primary amine extraction of the transition metals is most important from sulphate and phosphate solutions. The exceptions are those that readily form oxygen anions, *e.g.*, molybdate and pertechnetate. Extractions with tertiary amines and quaternaries (Fig. 4)

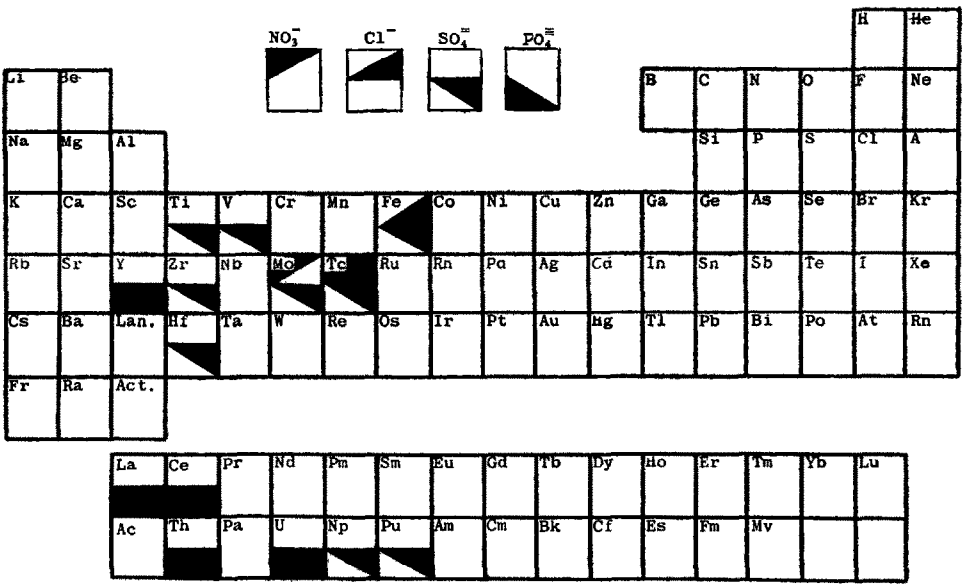


FIG. 3—Extractions with primary amines.

emphasise the nitrate and chloride solutions, but without excluding sulphate and phosphate. More detailed comparisons for some of the metals especially from sulphate solutions have been reported elsewhere,[11,32] correlating extraction coefficients with structure of individual reagents.

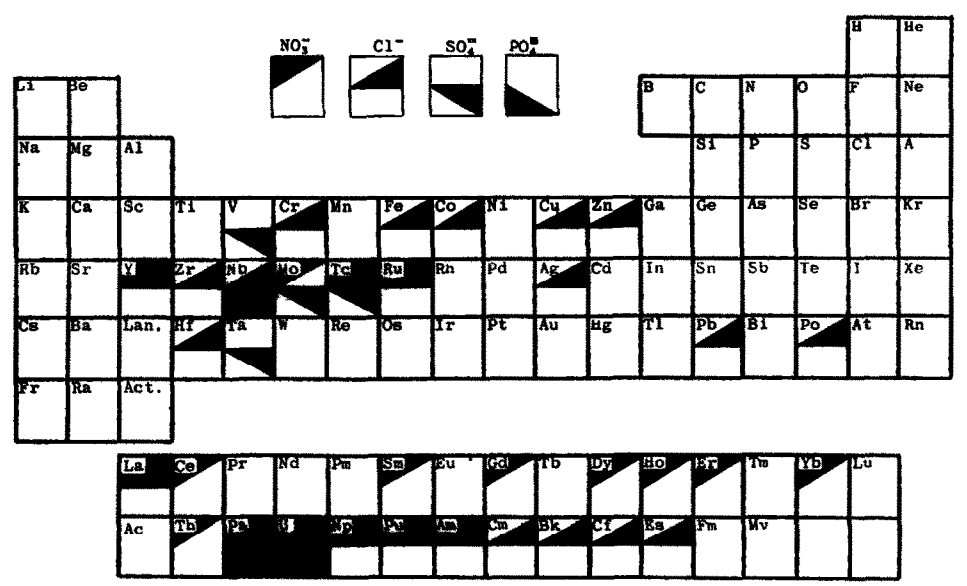


FIG. 4—Extractions with tertiary amines (and quaternary ammoniums)

TABLE I—LIQUID CATION EXCHANGE EXTRACTIONS

Element	Aqueous phase[a]	Extractant[c] (Type)[b]	Extractant[c] Acid/Diluent	Reference
Alkalis				
Li, Na, K, Cs	Nitrate	(H_2P)	DDPA/kerosene	24
		(H_2P)	HDPA/kerosene	24
Na	$CsNO_3$	(HP)	D2EHPA/kerosene	24
		(HP)	D2EHPA/Amsco 125-82	24
Na	Nitrate	(HP)	D2EHPA/benzene	5
Cs	Chloride	(HS)	Dinonylnaphthalene-sulphonic/ benzene	17
	Nitrate	(HS)	Dinonylnaphthalene-sulphonic/ Amsco 125-82	25
Alkaline earths				
Be	Nitrate, chloride, sulphate	(HP)	D2EHPA/cyclohexane	88
	Sulphate	(HP)	D2EHPA/kerosene	51
Ca	0·01*M* HCl	(HP)	D2EHPA/toluene	53
Be, Mg, Ca	Nitrate, perchlorate	(HCF)	Perfluoro-octanoic/ethers	63
Sr, Ba	Nitrate	(H_2P)	DDPA/kerosene	24
	Chloride	(HP)	D2EHPA/toluene	82
		(HP)	D2EHPA/Amsco 125-82	26
Sr		(HP)	D2EHPA/benzene	5
	Acetate	(HP)	D2EHPA/Amsco 125-82	24
	Acetate	(HP)	D2EHPA/hexanol-Amsco	62
	Perchlorate	(HCF)	Perfluoro-octanoic/CCl_4 + hexone	40
		(H_2P)	Various alkyl and aryl acids and	
		(HP)	acid esters	81
		(H_2Pn)		
		(HPn)		
	Nitrate	(HP)	D2EHPA + TBP/Amsco	111
Group III				
Al	HNO_3, pH > 1	(HP)	D2EHPA/Amsco 125-82	54
	Nitrate, perchlorate	(HCF)	Perfluoro-octanoic/ethers	63
	Sulphate	(H_2P)	M2EHPA/kerosene	14
		(H_2P)	DDPA/kerosene	14
		(H_2P)	Various monoalkylphosphoric acids/kerosene	45, 57
		(HP)	D2EHPA/kerosene	51

TABLE I—*Cont.*

Element	Aqueous phase[a]	Extractant[c] (Type)[b]	Extractant[c] Acid/Diluent	Reference
Rare earths				
Sc	HNO_3, pH <0	(HP)	D2EHPA/Amsco 125-82	54
	Chloride, perchlorate	(H_2P)	M2EHPA/toluene	78
		(H_2P)	Mono-octylphenylphosphoric/toluene	78
		(HP)	D2EHPA/toluene	78
		(HP)	Dioctylphenylphosphoric/toluene	78
	Perchlorate	(HCF)	Perfluoro-octanoic/CCl_4 + hexone	40
Sc, Y, La	Nitrate	(HPn)	Hydrogen 2-ethylhexylphenacyl-phosphonate/cyclohexanol	100, 101
		(H_2P)	Various monoalkylphosphoric acids/amyl alchol	102
Y	Nitrate, chloride, sulphate	(HP)	D2EHPA/cyclohexane	88
	Perchlorate	(HP)	DBP/$CHCl_3$	40
	Chloride	(HP)	D2EHPA/toluene	79
	Chloride, perchlorate	(H_2P)	M2EHPA/toluene	82
		(H_2P)	Mono-octylphenylphosphoric/toluene	78
		(HP)	DBP/toluene	77
		(HP)	D2EHPA/toluene	77
		(HP)	Dicyclohexylphosphoric/toluene	77
		(HP)	Dioctylphenylphosphoric/toluene	78
		(HP)	Diphenylphosphoric/toluene	77
	Chloride, sulphate	(HP)	D2EHPA/kerosene	23
La	HNO_3, pH >0·5	(HP)	D2EHPA/Amsco 125-82	54
Pr	HNO_3, pH >0·3	(HP)	D2EHPA/Amsco 125-82	54
Sm	HNO_3, pH >0·1	(HP)	D2EHPA/Amsco 125-82	54
Lanthanides[III]	Nitrate	(H_2P)(HP)	Several mono- and dialkylphosphoric acids/kerosene	23
		(HP)	D2EHPA/*n*-heptane	82
		(HP)	D2EHPA + TBP/Amsco	111
	Perchlorate	(HP)	DBP/dibutyl ether	39
		(HP)	DBP/$CHCl_3$	40
	Chloride	(H_2P)	M2EHPA/toluene	77
		(HP)	D2EHPA/toluene	77
	0·1–1*M* HCl	(HP)	D2EHPA/toluene	53
		(HS)	Dinonylnaphthalene-sulphonic/benzene	17
		(HP)	D2EHPA/toluene	79

	Chloride, perchlorate	(H_2P)	M2EHPA/toluene	78
		(H_2P)	Mono-octylphenylphosphoric/toluene	78
		(HP)	D2EHPA/toluene	78
		(HP)	Dioctylphenylphosphoric/toluene	77, 78
	Chloride, sulphate	(HP)	D2EHPA/kerosene	23
Ce^{IV}	Nitrate	(HP)	D2EHPA/*n*-heptane	82
		(HP)	D2EHPA/Amsco 125-82	23
	$10M$ HNO_3	(HP)	D2EHPA/*n*-heptane	59
	Sulphate	(HP)	D2EHPA/kerosene + 2-ethylhexanol	14
Actinides				
Ac	Perchlorate	(H_2P)	M2EHPA/toluene	78
		(H_2P)	Mono-octylphenylphosphoric/toluene	78
		(HP)	D2EHPA/toluene	78
		(HP)	Dioctylphenylphosphoric/toluene	78
Th^{IV}	$HClO_4$, HNO_3, HCl	(HP)	D2EHPA/toluene	80
		(HP)	Bis (*p*-tert-octylphenyl) phosphoric/ toluene	80
		(HP)	Bis (*p*-tert-octylphenyl) phosphoric + TBP/toluene	80
	Nitrate	(HP)	D2EHPA/cyclohexane	88
	$10M$ HNO_3	(HP)	D2EHPA/*n*-heptane	59
	Nitrate	(HC)	Salicylic or cinnamic/hexone	48
	Sulphate	(HP)	D2EHPA/kerosene + 2-ethylhexanol	14
	$3M$ H_2SO_4	(HP)	D2EHPA + DBBP/Amsco 125-82	49
Pa^{V}	$<10M$ HNO_3	(HP)	DBP/benzene	46
		(HP)	DBP + TBP/kerosene	46
		(HP)	D2EHPA/kerosene	46
U^{IV}	HCl	(H_2P)	M2EHPA/toluene	83
		(H_2P)	M2EHPA + TBP/toluene	83
	$<8M$ HCl	(HP)	D2EHPA/kerosene	15
		(HP)	D2EHPA + TBP/kerosene	15
	$3M$ H_2SO_4	(HP)	D2EHPA + DBBP/Amsco 125-82	49
	3–$5M$ H_3PO_4	(HP)	Bis(3,5,5-trimethylhexyl)phosphoric/ kerosene	12
		(HP)	Bis(di-isobutylmethyl)phosphoric/ kerosene	12
		(HP)	Bis(di-isobutylmethyl)phosphoric + Bu_3PO/kerosene	12
U^{VI}	Perchlorate	(HP)	D2EHPA/*n*-hexane	8
		(HP)	DBP/$CHCl_3$	40
		(HCF)	Perfluorobutyric/ethers	63

TABLE I—*Cont.*

Element	Aqueous phase[a]	Extractant[c] (Type)[b]	Extractant[c] Acid/Diluent	Reference
U^{VI}	Nitrate	(HP)	DBP/various diluents	46
	$\leqslant 6M$ HNO_3, $NaNO_3$	(HP)	D2EHPA/kerosene + 2-ethylhexanol	14
	$\leqslant 8M$ HNO_3	(HP)	D2EHPA + TBP/kerosene	15
	$10M$ HNO_3	(HP)	D2EHPA/*n*-heptane	59
	Nitrate	(HC)	Salicylic or cinnamic/kerosene	48
	Nitrate, chloride, sulphate	(HP)	D2EHPA/cyclohexane	88
	$6M$ HCl	(H_2P)	DDPA/kerosene	12
	$\leqslant 12M$ HCl	(H_2P)	M2EHPA/toluene	83
	$\leqslant 8M$ HCl	(HP)	D2EHPA/kerosene + 2-ethylhexanol	14
	$\leqslant 12M$ HCl	(HP)	D2EHPA + TBP/kerosene	15
		(HP)	D2EHPA + TBP/kerosene	12
	Sea-water	(HP)	DBP/CCl_4	96
		(HP)	D2EHPA/CCl_4	87
		(HP)	D2EHPA/CCl_4	64
	H_2SO_4	(H_2P)	Various monoalkylphosphoric acids/kerosene	45
	Sulphate, phosphate	(H_2P) (HP) (H_2Pn) (HPin)	Various combinations of acids, esters or R_3PO and diluents	11, 14, 15, 20, 88
	$0{\cdot}1M$ H_2SO_4	(HP)	DBP + TBP/CCl_4	41
	2–$5M$ H_2SO_4	(HP)	D2EHPA + DBBP/Amsco 125-82	49
	$\leqslant 8M$ H_2SO_4	(HP)	D2EHPA + TBP/kerosene	15
	$\leqslant 2M$ H_3PO_4	(H_2P) (HP)	Various combinations of acids and diluents	12, 14
		(HP)	D2EHPA + TBP/kerosene	15
Np^{VI}	$\leqslant 10M$ HNO_3	(HP)	D2EHPA/Amsco 125-82	105
	$\leqslant 12M$ HCl	(H_2P)	M2EHPA/toluene	83
		(H_2P)	M2EHPA + TBP/toluene	83
	$\leqslant 2{\cdot}5M$ H_2SO_4	(HP)	D2EHPA/Amsco 125-82	105
Np^{IV}	$10M$ HNO_3-$1M$ $KBrO_3$	(HP)	D2EHPA/*n*-heptane	59
	$<12M$ HCl	(H_2P)	M2EHPA/toluene	83
Pu^{III}[d]	$<8M$ HNO_3	(HP)	D2EHPA/Amsco 125-82	49
Pu^{IV}	$<10M$ HNO_3	(HP)	D2EHPA/Amsco 125-82	49
	$2M$ $UO_2(NO_3)_2$ + $1M$ HNO_3	(HP)	D2EHPA/Amsco 125-82	49
	3–$5M$ H_2SO_4	(HP)	D2EHPA/Amsco 125-82	49
		(HP)	D2EHPA + TOPO/Amsco 125-82	49
		(HP)	D2EHPA + DBBP/Amsco 125-82	49

Pu^{VI}	$4M$ HNO_3	(HP)	D2EHPA/Amsco 125-82	49
	$2–8M$ HNO_3	(HP)	D2EHPA/Amsco 125-82 + tridecanol	49
	$2–4M$ HNO_3	(HP)	D2EHPA + TOPO/Amsco 125-82	49
	$10M$ HNO_3 + $1M$ $KBrO_3$	(HP)	D2EHPA/*n*-heptane	59
	$5M$ H_2SO_4	(HP)	D2EHPA/Amsco 125-82	49
		(HP)	D2EHPA + TOPO/Amsco 125-82	49
Am^{III}	$0·1M$ HNO_3	(HP)	DBP/*n*-hexane or CCl_4	42
	Perchlorate, chloride	(H_2P)	M2EHPA/toluene	77, 78
		(H_2P)	Mono-octylphenylphosphoric/toluene	77, 78
		(HP)	D2EHPA/toluene	78, 79
Am, Cm, Bk, Cf	Nitrate, chloride	(HP)	Diphenylphosphoric/toluene	77
	HCl	(HPn)	2-Ethylhexylphenylphosphonic/diethylbenzene	9
		(HP)	D2EHPA/toluene	77
	Perchlorate	(HP)	Dioctylphenylphosphoric/toluene	77, 78
Cm^{III}	$8–10M$ HNO_3	(HP)	D2EHPA/*n*-heptane	84
	Chloride	(HP)	D2EHPA/toluene	77
Bk^{IV}	$8–10M$ HNO_3	(HP)	D2EHPA/*n*-heptane	84
Bk^{III}	$8–10M$ HNO_3	(HP)	D2EHPA/*n*-heptane	84
	Chloride	(HP)	D2EHPA/toluene	77
Cf, Es, Fm	Chloride	(HP)	DBP/toluene	77
		(HP)	D2EHPA/toluene	77
		(HP)	Diphenylphosphoric/toluene	77
		(HP)	Dioctylphenylphosphoric/toluene	77
		(HP)	Dicyclohexylphosphoric/toluene	77
Transition metals				
Ti^{IV}	Nitrate, chloride, sulphate	(HP)	D2EHPA/cyclohexane	88
	$0·5M$ HCl	(HP)	D2EHPA/toluene	53
	$0·5M$ Na_2SO_4	(HP)	D2EHPA/kerosene + 2-ethylhexanol	14
Zr^{IV}	Nitrate	(H_2P-HP)	MBP + DBP/dibutyl ether	89
	Nitrate, chloride, sulphate	(HP)	D2EHPA/cyclohexane	88
	HF in mixed acids, $+Al(NO_3)_3$	(HP)	DBP/$CHCl_3$	86
Zr-Nb[e]	Nitrate	(H_2P-HP)	MBP-DBP/dibutyl ether	89
	$10M$ HNO_3	(HP)	D2EHPA/*n*-heptane	59
Hf^{IV}	Perchlorate	(HP)	DBP/$CHCl_3$	40
V^{IV}	$0·5M$ Na_2SO_4	(HP)	D2EHPA/kerosene + 2-ethylhexanol	14, 37
	Sulphate	(H_2P)	Various monoalkylphosphoric acids/kerosene	45
Nb^{V}	Nitrate	(H_2P-HP)	MBP + DBP/dibutyl ether	89
	$1M$ HCl	(HP)	D2EHPA/toluene	53

TABLE I—*Cont.*

Element	Aqueous phase[a]	Extractant[c] (Type)[b]	Extractant[c] Acid/Diluent	Reference
Mo^{VI}	Nitrate, chloride, sulphate	(HP)	D2EHPA/cyclohexane	88
	10*M* HNO_3	(HP)	D2EHPA/*n*-heptane	59
	9*M* HCl	(HP)	D2EHPA/*n*-heptane	59
	0·5*M* HCl	(HP)	D2EHPA/toluene	53
	0·5*M* Na_2SO_4	(HP)	D2EHPA/kerosene + 2-ethylhexanol	14
Mn^{II}	Perchlorate	(HS)	Dinonylnaphthalene sulphonic/heptane	107
	HNO_3, pH >1·1	(HP)	D2EHPA/Amsco 125-82	54
	<0·01*M* HCl	(HP)	D2EHPA/toluene	53
Fe^{II}	Sulphate	(H_2P)	Various monoalkylphosphoric acids/kerosene	45, 57
Fe^{III}	Perchlorate	(HP)	D2EHPA/*n*-octane	7
		(HS)	Dinonylnaphthalene sulphonic/heptane	106, 107
	Perchlorate, chloride	(HCF)	Perfluorobutyric/ethers	63
		(HS)	Dinonylnaphthalene sulphonic/benzene	17
	HNO_3, pH <0	(HP)	D2EHPA/Amsco 125-82	54
	<10*M* HCl	(HP)	D2EHPA/toluene	53
	Nitrate, chloride, sulphate	(HP)	D2EHPA/cyclohexane	88
	0·5*M* Na_2SO_4	(H_2P)	DDPA/kerosene	14
		(HP)	D2EHPA/kerosene + 2-ethylhexanol	14
Ru^{III}	HNO_3, pH >1·3	(HP)	D2EHPA/Amsco 125-82	54
Os	<1*M* HCl	(HP)	D2EHPA/toluene	53
Co^{II}	Perchlorate	(HS)	Dinonylnaphthalene sulphonic/heptane	107
	HNO_3, pH >2	(HP)	D2EHPA/Amsco 125-82	54
Ni^{II}	HNO_3, pH >3	(HP)	D2EHPA/Amsco 125-82	54
Group B elements				
Ag^{I}	HNO_3, pH >2	(HP)	D2EHPA/Amsco 125-82	54
Au	10*M* HCl	(HP)	D2EHPA/toluene	53
Zn^{II}	Perchlorate	(HS)	Dinonylnaphthalene sulphonic/heptane	107
		(HCF)	Perfluoro-octanoic/ethers	63
	Perchlorate, chloride	(HS)	Dinonylnaphthalene sulphonic/benzene	17
	HNO_3, pH >0·9	(HP)	D2EHPA/Amsco 125-82	54
	<0·01*M* HCl	(HP)	D2EHPA/toluene	53

Cd^{II}	HNO_3, pH >1·2	(HP)	D2EHPA/Amsco 125-82	54
Hg^{I}	HNO_3, pH <0	(HP)	D2EHPA/Amsco 125-82	54
Ga^{III}	<0·1*M* HCl	(HP)	D2EHPA/toluene	53
In^{III}	Perchlorate	(HS)	Dinonylnaphthalene sulphonic/heptane	106, 107
	Nitrate, sulphate	(HP)	D2EHPA/cyclohexane	88
	HNO_3, pH <0	(HP)	D2EHPA/Amsco 125-82	54
	<1*M* HCl	(HP)	D2EHPA/toluene	53
Ge	8*M* HCl	(HP)	D2EHPA/toluene	53
Sn^{IV}	Nitrate, chloride	(HP)	D2EHPA/cyclohexane	88
Pb^{II}	Perchlorate	(HCF)	Perfluoro-octanoic/ethers	63
	0·01*M* HCl	(HP)	D2EHPA/toluene	53
Bi	<0·1*M* HCl	(HP)	D2EHPA/toluene	53

[a] Aqueous phase salts listed include neutral to moderately acidic solutions.

[b] Types of acid extractants: (H_2P) Monoalkylorthophosphoric (diacidic)
(HP) Dialkylorthophosphoric (monoacidic)
(H_2Pn) Monoalkylphosphonic
(HPn) Alkyl monoalkylphosphonic
(HPin) Dialkylphosphinic
(HS) Sulphonic
(HC) Carboxylic
(HCF) Perfluorocarboxylic

[c] Extractants are more fully identified in Table III.

[d] Extraction of plutonium present in the aqueous phase as Pu^{III} may involve oxidation to Pu^{IV} enhanced by strong stabilisation of Pu^{IV} by the extraction system.

[e] "Zr-Nb" refers to simultaneous extraction of fission-product or tracer zirconium and niobium, measured by γ-count without differentiation between the two.

TABLE II—LIQUID ANION-EXCHANGE EXTRACTIONS

Element	Aqueous phase[a]	Extractant[c] Class[b]	Extractant[c] Amine/Diluent	Reference
Rare earths				
Y^{III} and	NH_4NO_3, $Al(NO_3)_3$	(3)	TOA/Benzene	23, 32
Lanthanides^{III}	12*M* LiCl	(3)	TIOA/Xylene or CH_2Cl_2	70
	>10*N* LiCl-$AlCl_3$	(3)	Alamine 336/di-isopropylbenzene	103, 104
		(Q)	Tetra-*n*-heptyl/Amsco 125-82	103
	1*M* $(NH_4)_2SO_4$	(1)	Amine 21F81/benzene	32
	1–2*M* (SO_4^{2-} + PO_4^{3-})	(1)	Primene JM-T/kerosene	36
Y^{III}	7–8*M* NH_4SCN	(3)	MDOA/Xylene	71
Ce^{IV}	1*M* $(NH_4)_2SO_4$	(1)	Amine 21F81/benzene	32
		(1)	Primene JM-T/kerosene	32
Actinides				
Th^{IV}	1–6*M* HNO_3	(3)	TOA/benzene	29
	1–10*M* HNO_3	(3)	TOA/Xylene	52
	Basic aluminium nitrate	(3)	TIOA/Xylene	93, 109
	12*M* LiCl	(3)	TIOA/Xylene	70
	1*M* $(NH_4)_2SO_4$	(1)	Amine 21F81/benzene	32
	0·5*M* $(NH_4)_2SO_4$	(1)	Primene JM-T/kerosene	32
	0·3*M* (Na_2SO_4 + H_2SO_4)	(2)	Di-*n*-decyl/benzene	60
	1–2*M* (SO_4^{2-} + PO_4^{3-})	(1)	Primene JM-T/kerosene-tridecanol	36
		(2)	Di(tridecyl)/kerosene	36
Pa^{V}	6*M* HNO_3	(3)	TOA/benzene	46
		(3)	TOA/Xylene	52
	8*M* HCl	(2)	Amberlite LA-1/kerosene	50
	4–11*M* HCl	(3)	MDOA/Xylene	67, 68
	6*M* HCl	(3)	MDOA/$CHCl_3$	65
	~4*M* HCl	(3)	Tribenzyl/nitrobenzene	30
	0·5*M* H_2SO_4	(3)	MDOA/trichloroethylene	71
	~2*M* H_3PO_4	(3)	MDOA/trichloroethylene	66
U^{IV}	1–10*M* HNO_3	(3)	TOA/Xylene	52
	1*M* $(NH_4)_2SO_4$	(1)	Amine 21F81/benzene	32
		(2)	Dilauryl/benzene	32
	0·5*M* $(NH_4)_2SO_4$	(1)	Primene JM-T/kerosene	32
		(2)	Amine S-24/kerosene	32
	3*M* H_2SO_4	(1)	Primene JM-T/Amsco 125-82 + tridecanol	49
U^{VI}	6*M* HNO_3 + $NaNO_3$	(3)	TOA/Amsco D-95	32
	7*M* HNO_3	(3)	MDOA/Xylene	67

	6*M* HNO_3	(3)	TOA/Xylene	52
	1–5*N* $Al(NO_3)_3$ + 1*M* HNO_3	(3)	Alamine 336 or TLA/Amsco 125-82-tridecanol	33
	Basic aluminium nitrate	(3)	TIOA/Xylene	93
	3–12*M* HCl	(2)	Amberlite LA-1/kerosene	50
	>1*M* HCl	(3)	MDOA/Xylene	67
	4–10*M* HCl	(3)	TOA/Amsco D-95	32
	2–10*M* HCl	(3)	TIOA/Xylene or hexone	55, 68
U^{VI}	0·1–1*M* H_2SO_4	(3)	MDOA/Xylene	67
	0·005–2*M* (Na_2SO_4 + H_2SO_4)	(2)	Di-*n*-decyl/benzene	61
	0·005–1*M* (Na_2SO_4 + H_2SO_4)	(3)	TOA/benzene	1
	0·1–2*M* SO_4^{2-}, pH <0–3	(1) (2) (3)	(Many amine-diluent combinations, all classes)	19, 32
	3*M*(H_2SO_4 + Na_2SO_4)	(2)	NBHA/kerosene	49
	~0·3*M* H_3PO_4	(3)	MDOA/Xylene	67
	0·1–1*M* H_3PO_4	(3)	TOA/Amsco D-95	32
	1–2*M* (SO_4^{2-} + PO_4^{3-})	(1)	Primene JM-T/kerosene-tridecanol	36
		(2)	NBHA/kerosene	36
		(2)	Amberlite LA-1/kerosene	36
		(3)	Alamine 336 or TIOA/kerosene-tridecanol	36
	1–2*M* HF	(3)	MDOA/Xylene	67
	1–5*M* NaF	(3)	TOA/Amsco D-95	32
	2*M* HOAc (and other carboxylic acids)	(3)	MDOA/Xylene	67
	0·1–5*M* HOAc	(3)	TOA/Amsco D-95	32
	0·5–2*M* HOAc	(2)	Amberlite LA-1/hexone	69
		(3)	TIOA/Xylene	69
	0·2–1*M* Na_2CO_3	(Q)	B-104/Amsco G	20
	0·5*M* Na_2CO_3	(Q)	Aliquat 336/kerosene-tridecanol	34, 35
Np^{IV}	2–10*M* HNO_3	(3)	TOA/Xylene	92
	8*M* HNO_3	(2)	Ditridecyl/Xylene	105
	0·01–10*M* HNO_3	(3)	TIOA/Xylene	105
	2–6*M* $NaNO_3$	(3)	TIOA/Xylene	105
	2–8*M* HNO_3	(Q)	B-104/Xylene	105
	6*N* $Al(NO_3)_3$	(3)	Alamine 336 or TLA/Amsco 125-82-tridecanol	33
	1–5*M* H_2SO_4	(1)	Primene JM-T/Amsco 125-82	105
Np^{VI}	2–8*M* HNO_3	(3)	TIOA/Xylene	105
Pu^{III}[d]	6*N* $Al(NO_3)_3$	(3)	TIOA/Xylene	49
	3*M* H_2SO_4	(1)	Primene JM-T/Amsco 125-82-tridecanol	49
Pu^{IV}	6–11*M* HNO_3	(1)	Primene JM-T/Gulf Solvent BT	110
	6–11*M* HNO_3	(2)	Amberlite LA-1/Gulf Solvent BT-decanol	110

TABLE II—*Cont.*

Element	Aqueous phase[a]	Extractant[c] Class[b]	Extractant[c] Amine/Diluent	Reference
Pu^{VI}	$8M$ HNO_3	(3)	TIOA/Gulf Solvent BT-decanol	110
	$8M$ HNO_3	(Q)	Roccal/Gulf Solvent BT-decanol	110
	1–$12M$ HNO_3	(3)	TOA/Xylene	52, 92
	1–$4M$ HNO_3	(3)	TLA/Amsco-*n*-Octanol	108
	0·1 to $10M$ NO_3^-, acid to salt	(1), (2), (3), (Q)	(Many amine-diluent combinations, all classes)	49
	3–$6M$ HNO_3	(3)	Tris(3,5,5-trimethylhexyl)/Xylene	10
	$3M$ HNO_3	(Q)	Tetrabutylammonium/$CHCl_3$-benzene	97
	0·5–$3M$ [H_2SO_4 + $(NH_4)_2SO_4$]	(1), (2), (3)	(Various amine-diluent combinations)	49
Pu^{VI}	1–$14M$ HNO_3	(3)	TOA/Xylene	52
	2–$8M$ HNO_3	(1), (2), (3), (Q)	(Various amine-diluent combinations)	49
	6–$9M$ HCl	(3)	Tribenzyl/$CHCl_3$	67
	$5M$ HCl	(3)	TIOA/Xylene	68
	$1M$ HOAc	(3)	TIOA/Xylene	69
Am, Cm^{III}	$10M$ LiCl	(3)	TIOA/Xylene	70
Am, Cm, Bk, Cf, Es	$>10N$ LiCl-$AlCl_3$	(3)	Alamine 336/di-isopropylbenzene	9
		(Q)	Tetra-*n*-heptyl/Amsco 125-82	103
	$5M$ NH_4SCN	(3)	TOA/Xylene	92
Transition metals				
Ti^{IV}	$1M$ Na_2SO_4	(1)	Amine 21F81/Amsco D-95	72
		(2)	Dilauryl/Amsco D-95-octanol	72
	$0·5M$ Na_2SO_4	(1)	Amine 21F81/kerosene	72
Zr^{IV} (and Hf)	$>8M$ HCl	(3)	MDOA/Xylene	67
		(3)	TIOA/Xylene	68
		(3)	TOA/cyclohexane	31
	$1M$ Na_2SO_4	(1), (2), (3)	(Various amine-diluent combinations)	32

	0·1–1*M* H_2SO_4	(3)	TOA/kerosene-tridecanol	23
V^{III}	0·5*M* Na_2SO_4	(1)	Primene JM-T/kerosene	35
V^{V}	1*M* Na_2SO_4 (Strongly dependent on pH)	(1), (2), (3)	(Various amine-diluent combinations)	19
Nb^{V}	>6*M* HCl	(3)	MDOA/Xylene	56
		(3)	TIOA/Xylene	68
	11*M* HCl	(3)	Tribenzyl/$CHCl_3$	43
	1·5*M* H_2SO_4	(3)	MDOA/trichoroethylene	71
	4*M* H_2SO_4	(3)	Tribenzyl/CH_2Cl_2	43
	~2*M* H_3PO_4	(3)	MDOA/trichloroethylene	71
	Carboxylic acids	(3)	Tribenzyl/$CHCl_3$	43
Ta^{V}	>4·8*M* H_2SO_4	(3)	Tribenzyl/CH_2Cl_2	43
	Carboxylic acids	(3)	Tribenzyl/$CHCl_3$	43
Cr^{VI}	Aqueous H_2CrO_4	(3)	MDOA/$CHCl_3$	94
	6*M* HCl	(3)	Tribenzyl/$CHCl_3$	67
		(3)	TIOA/Xylene	68
Mo^{IV}	<1*M* HNO_3	(1), (2), (3)	(Various amine-diluent combinations)	99
Tc^{VII}	Aqueous Solutions (acid, neutral, or basic)	(Q)	B-104/kerosene	16
	Acid Solutions	(1), (2), (3), (Q)	(Various amine-diluent combinations)	16
	6*N* $Al(NO_3)_3$	(3)	Alamine 336 or TLA/Amsco 125-82-tridecanol	33
Fe^{III}	>1*M* HCl	(3)	MDOA/trichloroethylene	58
		(3)	TIOA/Xylene	68
	<1–12*M* HCl	(1), (2), (3)	(Various amines in $CHCl_3$ and in benzene)	44
	1*M* Na_2SO_4	(1)	Amine 21F81/Amsco D-95	32
	<0·5*M* Na_2SO_4 (strongly dependent on pH)	(2)	Di-*n*-decyl/benzene	6
Co^{II}	>6*M* HCl	(3)	MDOA/trichloroethylene	58
		(3)	TIOA/Xylene	68
		(3)	TOA/benzene	23
Ru^{IV}	2*M* HNO_3	(3)	TLA/toluene	70
	0·1–9*M* HCl	(3)	TIOA/Xylene	68

TABLE II—*Cont.*

Element	Aqueous phase[a]	Extractant[c] Class[b]	Amine/Diluent	Reference
"B Group" metals				
Cu^{II}	>4*M* HCl	(3)	MDOA/trichloroethylene	58
Ag^{I}	LiCl, HCl	(3)	MDOA/trichloroethylene	90
Zn^{II}	>1*M* HCl	(3)	MDOA/Xylene	58, 68
		(3)	Tribenzyl/$CHCl_3$	58
	2*M* HCl	(3)	TIOA/hexone	91
	LiCl, HCl	(3)	MDOA/trichloroethylene	90
Pb^{II}	1·5*M* HCl	(Q)	Aliquat 336/benzene	85
Nonmetals				
Po^{IV}	6*M* HCl	(3)	Tribenzyl/$CHCl_3$	67
N	HNO_3	(3)	Tris(3,5,5-trimethylhexyl)/Xylene	10
		(2)	Amine S-24, Amberlite LA-1, ditridecyl/Xylene	49
		(1)	Primene JM-T/Xylene	49
S	H_2SO_4	(2)	Di-*n*-decyl/benzene	3
		(3)	TOA/benzene	2
Cl	HCl	(3)	TIOA/toluene	76
Br	HBr	(3)	MDOA/trichloroethylene	90

[a] Aqueous phase salts listed include neutral to moderately acidic solutions.

[b] Classes of amines: (1) Primary
(2) Secondary
(3) Tertiary
(Q) Quaternary ammonium

[c] Extractants are more fully identified in Table III.

[d] Extractions of plutonium present in the aqueous phase as Pu^{III} may involve oxidation to Pu^{IV} enhanced by strong stabilisation of Pu^{IV} by the extraction system.

TABLE III—REAGENTS

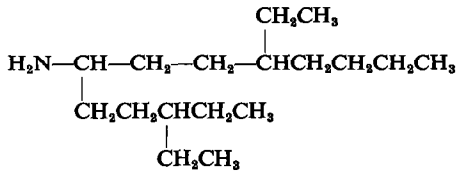
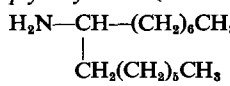
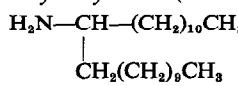
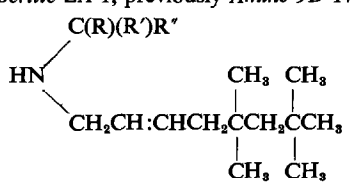
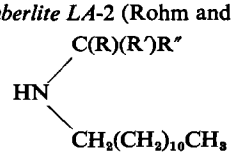
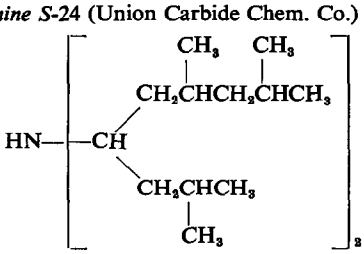
Class or type[a]	*Amines*
(1)	*Amine* 21*F*81, 1-(3-Ethylpentyl)-4-ethyloctylamine (Union Carbide Chem. Co.) 
(1)	*Primene JM-T* (Rohm and Haas Co.) $H_2N—C(R)(R')R''$ trialkylmethylamine; $R + R' + R'' = 17–23$ carbon atoms.
(1)	1-*Heptyloctylamine* (Armour Chemical Division) 
(1)	1-*Undecyllaurylamine* (Armour Chemical Division) 
(2)	*Amberlite LA*-1, previously *Amine* 9*D*-178 (Rohm and Haas Co.)  N-dodecenyl(trialkylmethyl)amine; $R + R' + R'' = 11–14$ carbon atoms.
(2)	*Amberlite LA*-2 (Rohm and Haas Co.)  N-Lauryl(trialkylmethyl)amine; $R + R' + R'' = 11–14$ carbon atoms.
(2)	*Amine S*-24 (Union Carbide Chem. Co.) bis(1-isobutyl-3,5-dimethylhexyl)amine 
(2)	*Di-n-decylamine* (Eastman Organic Chemicals, No. p7724) $HN—[—(CH_2)_9CH_3]_2$
(2)	*Ditridecylamine* (Union Carbide Chem. Co.) $HN—[—CH_2CH_2CH_2—C_{10}H_{21}]_2$ "Tridecyl" = Mixture of 13-carbon alkyls from tetrapropylene

TABLE III—*Cont.*

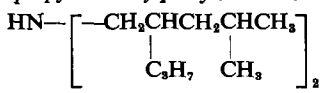
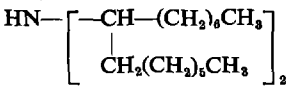
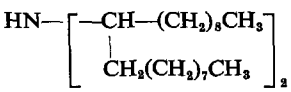
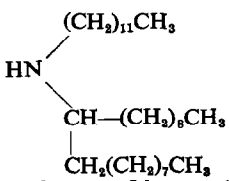
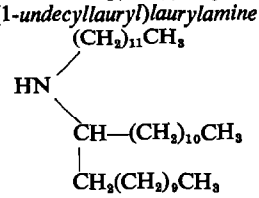
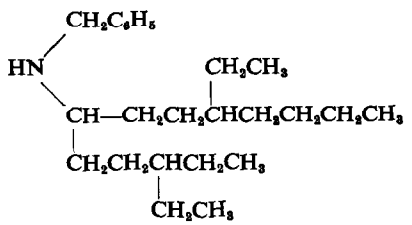
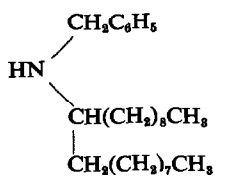
Class or type	*Amines*
(2)	*Dilaurylamine* (Eastman Organic Chemicals, No. p4519) $HN—[—(CH_2)_{11}CH_3]_2$
(2)	*Di*(2-*propyl*-4-*methylpentyl*)*amine* (Eastman Chemical Products) 
(2)	*Di*(1-*heptyloctyl*)*amine* (Armour Chemical Division) 
(2)	*Di*(1-*nonyldecyl*)*amine* (Armour Chemical Division) 
(2)	*N*-(1-*nonyldecyl*)*laurylamine* (Armour Chemical Division) 
(2)	*N*-(1-*undecyllauryl*)*laurylamine* (Armour Chemical Division) 
(2)	*NBHA*, N-benzylheptadecylamine (Union Carbide Chem. Co.) N-benzyl-1-(3-ethylpentyl)-4-ethyloctylamine. 
(2)	*N-Benzyl*-(1-*nonyldecyl*)*amine* (Armour Chemical Division) 

TABLE III—*Cont.*

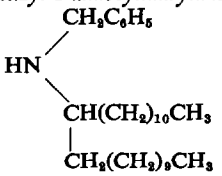
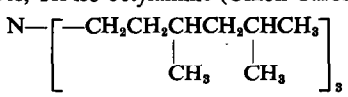
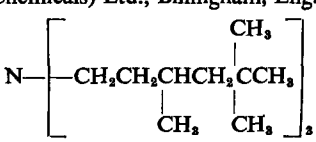
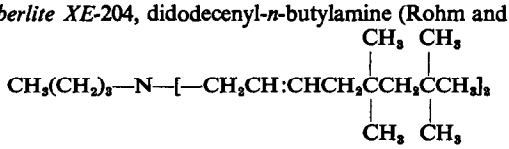
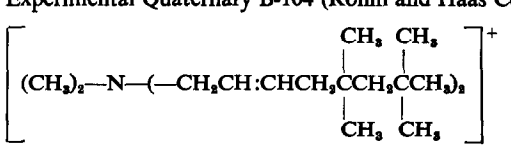
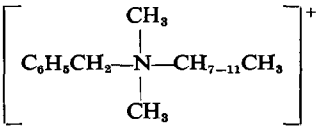
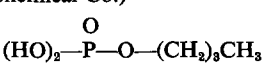
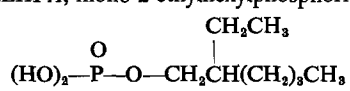
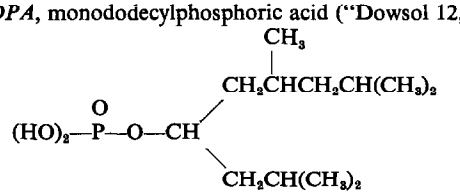
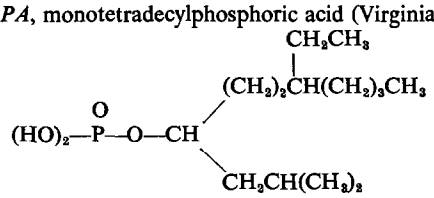
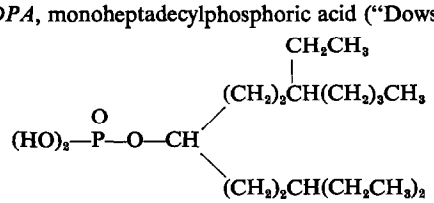
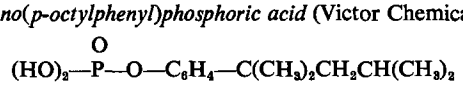
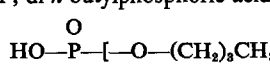
Class or type	*Amines*
(2)	*N-Benzyl-1-undecyllaurylamine* (Armour Chemical Division) 
(3)	*TLA*, trilaurylamine (Archer-Daniels-Midland Co.; General Mills, Inc.; Eastman Organic Chemicals, No. 7727) $N—[—(CH_2)_{11}CH_3]_3$
(3)	*Alamine* 336 (General Mills, Inc.) $N—[—(CH_2)_{7-11}CH_3]_3$ straight chain alkyls, principally octyl and decyl.
(3)	*TOA*, tri-*n*-octylamine (Eastman Organic Chemicals, No. P7723) $N—[—(CH_2)_7CH_3]_3$
(3)	*TIOA*, Tri-iso-octylamine (Union Carbide Chem. Co.)  "iso-octyl" = mixture of dimethylhexyls and methylheptyls, *etc.*, principally 3,5-, 4,5-, and 3,4-dimethylhexyl.
(3)	*Tri-isononylamine*, trist(3,5,5-trimethylhexyl)amine [I.C.I. (Heavy Organic Chemicals) Ltd., Billingham, Eng.] 
(3)	*Amberlite XE-204*, didodecenyl-*n*-butylamine (Rohm and Haas Co.) 
(3)	*Butyldilaurylamine* (Laboratory preparation) $CH_3(CH_2)_3—N—[—(CH_2)_{11}CH_3]_2$
(3)	*Tribenzylamine* (Eastman Organic Chemicals, No. 1015) $N—[—CH_2C_6H_5]_3$
(Q)	*Aliquat* 336 (General Mills, Inc., as chloride) $[CH_3—N—(—(CH_2)_{7-11}CH_3)_3]^+$ Trialkylmethyl ammonium, straight chain alkyls, principally octyl and decyl.
(Q)	*B*-104, Experimental Quaternary B-104 (Rohm and Haas Co., as chloride)  Dimethyl-didodecenylammonium.

TABLE III—*Cont.*

Class or type	*Amines*
(Q)	*Roccal*, (Sterwin Chemicals, Inc., as chloride) 
(Q)	*Tetrabutylammonium* (Eastman Organic Chemicals, No. 7377, as bromide) $[N—(—(CH_2)_3CH_3)_4]^+$
(Q)	*Tetra-n-heptylammonium* (Eastman Organic Chemicals, No. 7630, as iodide) $[N—(—(CH_2)_6CH_3)_4]^+$
	Acids
(H_2P)	*MBP*, mono-*n*-butylphosphoric acid (Victor Chemical Corp., Montsanto Chemical Co.) 
(H_2P)	*M2EHPA*, mono-2-ethylhexylphosphoric acid (Victor Chemical Co.) 
(H_2P)	*DDPA*, monododecylphosphoric acid ("Dowsol 12," Dow Chemical Co.) 
(H_2P)	*TDPA*, monotetradecylphosphoric acid (Virginia-Carolina Chem. Corp.) 
(H_2P)	*HDPA*, monoheptadecylphosphoric acid ("Dowsol 17," Dow Chemical Co.) 
(H_2P)	*Mono(p-octylphenyl)phosphoric acid* (Victor Chemical Co.) 
(HP)	*DBP*, di-*n*-butylphosphoric acid (Victor Chemical Co., Monsanto Chemical Co.) 

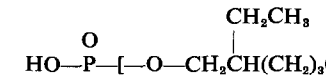
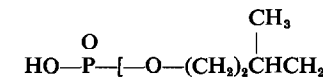
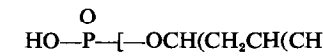
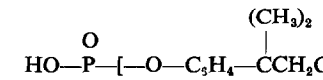
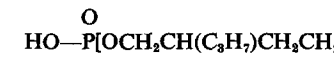
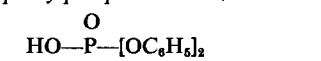
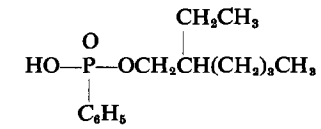
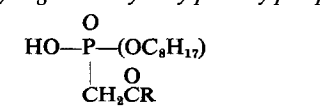
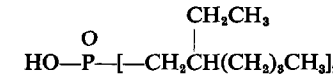
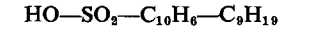
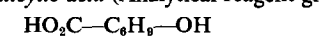
Class or type	*Acids*
(HP)	*D2EHPA*, di(2-ethylhexyl)phosphoric acid (Union Carbide Chemicals Co., Virginia Carolina Chemical Corp., Victor Chemical Co.) 
(HP)	*Bis*(3,5,5-*trimethylhexyl*)*phosphoric acid* (Laboratory preparation) 
(HP)	*Bis*(*di-isobutylmethyl*)*phosphoric acid* (Laboratory preparation) 
(HP)	*Dicyclohexylphosphoric acid* (Laboratory preparation) 
(HP)	*Bis*(*p-tert-octylphenyl*)*phosphoric acid* (Victor Chemical Co.) 
(HP)	*Di*(2-*ethyl*-4-*methylpentyl*)*phosphoric acid* (Eastman Chemical Products, Inc.) 
(HP)	*Di*(2-*propyl*-4-*methylpentyl*)*phosphoric acid* (Eastman Chemical Products, Inc.) 
(HP)	*Diphenylphosphoric acid* (Laboratory preparation) 
(HPn)	2-*Ethylhexyl phenylphosphonic acid* (Laboratory preparation) 
(HPn)	*Hydrogen* 2-*Ethylhexylphenacylphosphonate* (Laboratory preparation) 
(HPin)	*Di*(2-*ethylhexyl*)*phosphinic acid* (Laboratory preparation) 
(HS)	*Dinonylnaphthalene sulphonic acid* (mixed isomers) (R. T. Vanderbilt Co., Inc.; King Organic Chemicals, Inc.) 
(HC)	*Salicylic acid* (Analytical reagent grade) 

TABLE III.—*Cont.*

Class or type	*Acids*
(HC)	*p-Methoxybenzoic acid* (analytical reagent grade) $HO_2C—C_6H_4—OCH_3$
(HC)	*Trans-cinnamic acid* (analytical reagent grade) $HO_2C—CH{:}CH—C_6H_5$
(HCF)	*Perfluorobutyric acid* (Minnesota Mining and Mfg. Co.) $HO_2C(CF_2)_2CF_3$
(HCF)	*Perfluoro-octanoic acid* (Minnesota Mining and Mfg. Co.) $HO_2C(CF_2)_6CF_3$ (Also nearly-perfluoro analogs, e.g. $HO_2C(CF_2)_6CF_2H$.)
	Neutral Co-Reagents
	TBP, tri-*n*-butyl phosphate (Commercial Solvents Corp.) $OP—[—O—(CH_2)_3CH_3]_3$
	DBBP, di-*n*-butyl *n*-butylphosphonate (Hooker Chemical Corp., Virginia-Carolina Chemical Corp.) $OP(—[—O—(CH_2)_3CH_3]_2)(—(CH_2)_3CH_3)$
	Bu_3PO, tri-*n*-butylphosphine oxide (Laboratory preparation) $OP—[—(CH_2)_3CH_3]_3$
	TOPO, tri-*n*-octylphosphine oxide (Eastman Organic Chemicals, No. 7440) $OP—[—(CH_2)_7CH_3]_3$

[a] Class of amine or type of acid extractant:

(1) Primary amine	(H_2P) Monoalkylorthophosphoric acid
(2) Secondary	(HP) Dialkylorthophosphoric
(3) Tertiary	(H_2Pn) Monoalkylphosphonic
(Q) Quaternary Ammonium	(HPin) Dialkylphosphinic
	(HPn) Alkyl monoalkylphosphonic
	(HS) Sulphonic
	(HC) Carboxylic
	(HCF) Perfluorocarboxylic

COMPARISON OF LIQUID AND RESINOUS ION EXCHANGE

Liquid ion-exchange extractions have been compared with resinous ion-exchange sorption from the time of the first reported acid extraction by amines.[94] The behaviour of analogous functional groups in the two systems is usually similar, at least as a scoping approximation. This is useful, because it allows some prediction of extractions on the basis of the extensively recorded sorption data. At the same time, details of the extraction behaviour can differ markedly from the sorption behaviour, and the extractions can differ significantly with individual structures within a single type of extractant. Resin sorption gives a good suggestion of the nature of the extraction, but not of the wide range of extraction levels available. Another degree of control of extraction level is available through the reagent concentration, and still another in choice of diluent.[11,32] Extraction by mixed extractants can be either enhanced, as in

the now well-known synergistic uranium extraction by mixtures of dialkylphosphoric acids with phosphorus esters or phosphine oxides, or impaired, as in the extraction of some other metal ions by those same mixtures.[15] These controls of extraction level are, of course, in addition to controls by adjustment of aqueous composition and pH, which are applicable to both sorption and extraction.

Selectivity

High selectivity for a desired ion can often be more important than high extraction power. Here again, the aqueous phase controls (competitive complexing, *etc.*) apply to liquid ion exchange as well as to other extraction systems and to resin sorption. Control is also available through choice of reagent type and structure, combination of reagents, choice of diluent, reagent concentration when power dependences are different, and in some cases time of contact.

Valency adjustment may be available as one of the means to control selectivity, or again separation of the different valency state species may be an objective. Vanadium, for example, is indicated in Figs. 2–4 to be extracted by both amines and organophosphorus acids. However, it is extracted (from sulphate solutions) in ter- and quinquevalent forms by primary amines, in the quinquevalent form only by secondary and tertiary amines, and in the quadrivalent form only by dialkylphosphoric acid. Actinides are extracted much more strongly in their quadrivalent forms than in their sexa-, ter- or quinquevalent forms, by primary amines from sulphate solutions, by tertiary amines from nitrate solutions, or by dialkylphosphoric acid from either. $Iron^{III}$ sulphate is extracted strongly by acids and by primary but not tertiary amines, $iron^{III}$ nitrate extraction is higher with acids but lower with amines, and $iron^{II}$ extraction is lower with all of the extractants.

Combination of TBP (*etc.*) with D2EHPA synergistically enhances its extraction power for uranium, but has little effect on the extraction power for vanadium, aluminium, molybdenum, and decreases the extraction power for iron, titanium, and thorium. Thus, the synergistic combination greatly increases the selectivity for uranium, and also changes separation factors significantly (*e.g.* $\times 2$) between some pairs of the other metals.[15] In the uranium extraction the TBP is presumably an active complexer; it might be affecting the other extractions merely by changing the medium effects of the diluent.

Choice of diluent supplements choice of reagent structure in control of extraction power and hence (since different extractions can be affected to different extents) in control of selectivity. For example, di(tridecyl)amine, a moderately branched secondary, is one of the commercial amines used in recovery of uranium from leach liquors. It extracts an objectionable quantity of $iron^{III}$ if its diluent is plain kerosene, but not if some tridecanol is added. The uranium/iron separation factor was increased $\times 4$ by the addition of 5% tridecanol to the kerosene.[21] Alternative methods for accomplishing this improvement in laboratory extraction, more or less suitable according to other requirements to be met, would include shift to an aromatic hydrocarbon diluent, or shift to a more highly branched secondary or a tertiary amine. For a parallel example involving simple instead of complex ions, the selectivity for normal sulphate over bisulphate from dilute aqueous sulphuric acid solution is low in extraction with tri-*n*-octylamine in benzene, but can be increased either by shift from tri-*n*-octyl- to di-*n*-decylamine or by shift from benzene to chloroform diluent.[22] Selectivity

control by choice of reagent structure and of diluent can be even more useful in analytical separations than in chemical processing, since many diluents like chloroform, nitrobenzene, *etc.*, impracticable for large-scale processing, are entirely feasible for laboratory bench work, and many reagents examined and rejected for processing use because of excessive loss, insufficient extraction power, *etc.*, still warrant consideration under the different requirements of analytical use. One example, tribenzylamine, has already found considerable use (Table II), and it may be predicted that the sterically-hindered tris(2-ethylhexyl)amine, another "process reject"[32] will prove to be particularly effective in special applications. Even the long, unbranched primary amines which typically gave precipitates or emulsions in systems pertinent to chemical processing may behave well in some other types of diluents, and may be expected to offer usefully different selectivites as suggested by extension of the class-and-branching patterns observed with other amines.[32]

Some metal ions are extracted only slowly by D2EHPA and other phosphorus acids, including iron^{III}, aluminium, manganese^{II}, ruthenium^{III}, scandium and indium^{III}.[14,54] (Comparison of transfer in both directions serves to prove complete equilibration when there is a question.) While the possibility of slow equilibrations is a complication, and can be a danger if ignored, it also provides an additional means of controlling selectivity.

Stripping

The liquid ion-exchange systems usually offer one or more means of readily stripping the extracted metal ions, more easily and into smaller volumes than is typical for elution from resins. The simple amines lose their anion-exchange capacity and are completely stripped of most solutes on contact with any aqueous solution at pH ~4 or higher. Specific systems also give high stripping coefficients in many cases, *e.g.*, stripping of uranium with dilute nitrate after extraction as sulphate. Correspondingly, cation-exchange solutes are effectively stripped by acid in some cases, *e.g.*, stripping of strontium from D2EHPA at pH ~1 or lower after extraction at pH ~5. In other cases the selectivity for metal ion over hydrogen ion is too high for stripping at moderate acid concentrations, as in extraction of uranyl ion by D2EHPA. Here, stripping with sodium carbonate is highly effective, combining displacement by the sodium ion with aqueous-phase complexing of the stripped solute.

Determinations using the organic extract instead of an aqueous solution (colorimetric, flame photometric) can obviate the need for a stripping step, giving a shorter procedure and sometimes higher sensitivity. This also provides another means for separation when more than one metal ion is extracted, *i.e.*, by stripping one while retaining another for determination in the organic phase.

Zusammenfassung—Es wurde eine Übersicht—mit vielen, typischen Beispielen—über den Extrahierungen mit Alkylaminen oder mit quatärneren Ammonium-verbindungen (flüssiger Anionaustausch) und mit Organophosphorigesaüren (flüssiger Kationaustausch) dargestellt. Im Falle einigen, typischen Systemen auch die Kontrollierende Variablen wurden discutiert.

Résumé—La méthode d'extraction effectuée en milieu liquide par l'échange de l'anion aves les alkylamines ou avec les ammoniums quaternaires, et par l'échange du cation avec les acides organophosphores en particulier, a été développée intensivement dans la chimie industrielle. Jusqu'ici cette méthode, paraît-il, est peu utilisée dans la chimie analytique. Cela est du sans doute au hasard ou à l'habitude, et l'on suggère que l'échange de l'ion en milieu liquide a une utilité potentielle qui exige l'attention des chimistes analytiques. Ceux-ci pourraient bien profiter de certains avantages dout

l'importance a été évidente dans l'industrie. Si l'on ajoute aux rapports analytiques les applications industrielles et physicochimiques on dispose d'une série considérable d'extractions qui servira a suggérer et a diriger des développements plus étendus. Les auteurs présentent une compilation représentative d'extractions de ce genre et examinent les variables importantes dans quelques systèmes typiques de l'ion échange en milieu liquide.

REFERENCES

[1] K. A. Allen, *J. Amer. Chem. Soc.*, 1958, **80,** 4133.
[2] *Idem, J. Phys. Chem.*, 1956, **60,** 239.
[3] *Idem, ibid.*, 1956, **60,** 943.
[4] K. A. Allen and W. J. McDowell, *The Thorium Sulphate Complexes from Di-n-Decylamine Sulphate Extraction Equilibrium.* Abstract 71, p. 29S, 138th Meeting, A.C.S., New York, September 1960.
[5] *Idem,* Oak Ridge National Laboratory, AEC Rept. ORNL-CF-61-1-106, p. 45, 1961.
[6] C. F. Baes, *ibid.*, ORNL-1930, 1955.
[7] C. F. Baes and H. T. Baker, *J. Phys. Chem.*, 1960, **64,** 89.
[8] C. F. Baes, R. A. Zingaro and C. F. Coleman, *ibid.*, 1958, **62,** 129.
[9] R. D. Baybarz and Boyd Weaver, Oak Ridge National Laboratory, AEC Repts. ORNL-3185 (in preparation); ORNL-3156, p. 25, 1961.
[10] U. Bertocci, Atomic Energy Research Establishment, Harwell, England, Rept. AERE R-2933, 1959.
[11] C. A. Blake, *et al.*, Proc. International Conference on Peaceful Uses of Atomic Energy, 1958, **28,** 289, P/1550, U.N., Geneva.
[12] *Idem,* Oak Ridge National Laboratory, AEC Rept. ORNL-2172, 1956.
[13] C. A. Blake, C. F. Baes and K. B. Brown, *Ind. Eng. Chem.*, 1958, **50,** 1763.
[14] C. A. Blake, K. B. Brown and C. F. Coleman, Oak Ridge National Laboratory, AEC Rept. ORNL-1903, 1955.
[15] C. A. Blake, D. E. Horner and J. M. Schmitt, *ibid.*, AEC Rept. ORNL-2259, 1959.
[16] G. E. Boyd and Q. V. Larson, *J. Phys. Chem.*, 1960, **64,** 988.
[17] G. E. Boyd and S. Lindenbaum, Oak Ridge National Laboratory, AEC Rept. ORNL-2782, p. 44, 1959.
[18] J. A. Brothers, R. G. Hart and W. G. Mathers, *J. Inorg. Nuclear Chem.*, 1958, **7,** 85.
[19] K. B. Brown, *et al.*, Oak Ridge National Laboratory, AEC Rept. ORNL-1734 (AECD-4142), 1954.
[20] *Idem, ibid.*, ORNL-2269, 1957; ORNL-2366, 1957.
[21] *Idem, ibid.*, ORNL-2306, p. 12, 1957.
[22] *Idem, ibid.*, ORNL-2399, p. 28, 1957.
[23] *Idem, ibid.*, ORNL-2346, 1957.
[24] *Idem, ibid.*, ORNL-2466, 1958.
[25] *Idem, ibid.*, ORNL-CF-60-5-114, p. 40, 1960.
[26] *Idem, ibid.*, ORNL-CF-60-11-126, p. 34, 1961.
[27] T. A. Butler and E. E. Ketchen, *Ind. Eng. Chem.*, 1961, **53,** 651.
[28] L. R. Bunney, E. N. Ballou, J. Pascual and S. Foti, U.S. Naval Radiological Defense Laboratory, Rept. USNDRL TR-228, 1958.
[29] D. J. Carswell and J. J. Lawrance, *J. Inorg. Nuclear Chem.*, 1959, **11,** 69.
[30] A. T. Casey and A. G. Maddock, *ibid.*, 1959, **10,** 289.
[31] E. Cerrai and C. Testa, *Energia Nucleare*, 1959, **6,** 707 and 768.
[32] C. F. Coleman, K. B. Brown, J. G. Moore and D. J. Crouse, *Ind. Eng. Chem.*, 1958, **50,** 1756.
[33] C. F. Coleman, F. A. Kappelmann and B. Weaver, *Nuclear Sci. Eng.*, 1960, **8,** 507.
[34] D. J. Crouse, Oak Ridge National Laboratory, in AEC Rept. ORNL-CF-60-3-136, p. 7, 1960.
[35] D. J. Crouse, *et al.*, *ibid.*, ORNL-2099, 1956.
[36] D. J. Crouse and K. B. Brown, *Ind. Eng. Chem.*, 1959, **51,** 1461.
[37] *Idem,* Oak Ridge National Laboratory, AEC Rept. ORNL-2820, 1959.
[38] R. W. Durham and R. Mills, Atomic Energy of Canada Ltd., Rept. CE 1-62 (September 29, 1953); cited by R. G. Hart *et al.*, Rept. CRDC-818 (AECL-755), 1958.
[39] G. Duyckaerts, Ph. Dréze and A. Simon, *J. Inorg. Nuclear Chem.*, 1960, **13,** 333.
[40] D. Dyrssen, *ibid.*, 1958, **8,** 291.
[41] D. Dyrssen and L. Kuca, *Acta Chem. Scand.*, 1960, **14,** 1945.
[42] D. Dyrssen and Liem Djiet Hay, *ibid.*, 1960, **14,** 1100.
[43] J. Y. Ellenburg, G. W. Leddicotte and F. L. Moore, *Analyt. Chem.*, 1954, **26,** 1045.
[44] Mary L. Good and Sara E. Bryan, *J. Amer. Chem. Soc.*, 1960, **82,** 5636.
[45] R. R. Grinstead, K. G. Shaar and R. S. Long, Proc. International Conference on Peaceful Uses of Atomic Energy, 1956, **8,** 71-76, P/523, U.N., Geneva.

[46] C. J. Hardy, D. Scargill and J. M. Fletcher, *J. Inorg. Nuclear Chem.*, 1958, **7**, 257; C. J. Hardy, Atomic Energy Research Establishment, Harwell, England, Rept. AERE-R 3267, 1960.
[47] C. E. Higgins, W. H. Baldwin and J. M. Ruth, Oak Ridge National Laboratory, AEC Rept. ORNL-1338, 1952.
[48] B. Hök-Bernström, *Acta Chem. Scand.*, 1956, **10**, 163.
[49] D. E. Horner and C. F. Coleman, Oak Ridge National Laboratory, AEC Repts. ORNL-2830, 1959; ORNL-3051, 1961.
[50] F. Ichikawa and S. Urono, *Bull. Chem. Soc. Japan*, 1960, **33**, 569.
[51] S. R. Isaacs, *et al.*, National Chemical Laboratory, Teddington, England, Rept. NCl/AE 199, 1960.
[52] W. E. Keder, J. C. Sheppard and A. S. Wilson, *J. Inorg. Nuclear Chem.*, 1960, **12**, 327.
[53] Kan Kimura, *Bull. Chem. Soc. Japan*, 1960, **33**, 1038; 1961, **34**, 63.
[54] E. Lamb, Oak Ridge National Laboratory, AEC Rept. ORNL-CF-60-6-132, p. 6, 1960.
[55] P. G. Laux and E. A. Brown, National Lead Co. of Ohio, AEC Rept. TID-7568, Part I, p. 135, 1958.
[56] G. W. Leddicotte and F. L. Moore, *J. Amer. Chem. Soc.*, 1952, **74**, 1618.
[57] C. J. Lewis and E. H. Crabtree, *Mining Cong. J.*, 1958, **44**, 65.
[58] H. A. Mahlman, G. W. Leddicotte and F. L. Moore, *Analyt. Chem.*, 1954, **26**, 1939.
[59] J. J. McCown and R. P. Larsen, *ibid.*, 1960, **32**, 597.
[60] W. J. McDowell and K. A. Allen, *Thorium Extraction by Di-n-decylamine Sulphate in Benzene.* Abstract 70, p. 28S, 138th Meeting, A.C.S., New York, September 1960; *J. Phys. Chem.*, 1961, **65**, 1358.
[61] W. J. McDowell and C. F. Baes, *J. Phys. Chem.*, 1958, **62**, 777.
[62] R. E. McHenry and J. C. Posey, *Ind. Eng. Chem.*, 1961, **53**, 647.
[63] G. F. Mills and H. B. Whetsel, *J. Amer. Chem. Soc.*, 1955, **77**, 4690.
[64] G. W. C. Milner, J. D. Wilson, G. A. Barnett and A. A. Smales, Atomic Energy Research Establishment, Harwell, England, Rept. AERE-R-3227, 1960.
[65] F. L. Moore, *Analyt. Chem.*, 1955, **27**, 70.
[66] F. L. Moore and S. A. Reynolds, *ibid.*, 1957, **29**, 1596.
[67] *Idem, ibid.*, 1957, **29**, 1660.
[68] *Idem, ibid.*, 1958, **30**, 908.
[69] *Idem, ibid.*, 1960, **32**, 1075.
[70] *Idem, ibid.*, 1961, **33**, 748.
[71] F. L. Moore, *Liquid-Liquid Extraction with High-Molecular-Weight Amines.* National Academy of Sciences, Nuclear Science Series, NAS-NS-3101, 1960.
[72] J. G. Moore, K. B. Brown and C. F. Coleman, Oak Ridge National Laboratory, AEC Rept. ORNL-1922 (AECD-4145), 1955.
[73] R. L. Moore, Hanford Engineering Works, AEC Rept. HW-15453, 1953.
[74] G. H. Morrison and Henry Freiser, *Analyt. Chem.*, 1958, **30**, 632.
[75] *Idem, ibid.*, 1960, **32**, 37R.
[76] John C. Peak, Massachusetts Inst. of Technology, Thesis, 1959.
[77] D. F. Peppard, G. W. Mason, W. J. Driscoll and S. McCarty, *J. Inorg. Nuclear Chem.*, 1959, **12**, 141.
[78] D. F. Peppard, G. W. Mason, W. J. Driscoll and R. J. Sironen, *ibid.*, 1958, **7**, 276.
[79] D. F. Peppard, G. W. Mason, J. L. Maier and W. J. Driscoll, *ibid.*, 1957, **4**, 334.
[80] D. F. Peppard, G. W. Mason and S. McCarty, *ibid.*, 1960, **13**, 138.
[81] *Idem, Extraction of Tracer-Level Strontium and Yttrium by Acidic Phosphorus Esters.* Abstract 110, p. 39*M*, 138th Meeting, A.C.S., New York, September, 1960.
[82] D. F. Peppard, G. W. Mason and S. W. Moline, *J. Inorg. Nuclear Chem.*, 1957, **5**, 141.
[83] D. F. Peppard, G. W. Mason and R. J. Sironen, *ibid.*, 1959, **10**, 117.
[84] D. F. Peppard, S. W. Moline and G. W. Mason, *ibid.*, 1957, **4**, 334.
[85] H. G. Petrow and R. Lindstrom, *Analyt. Chem.*, 1961, **33**, 313.
[86] R. F. Rolf, *ibid.*, 1961, **33**, 125.
[87] E. Rona, L. O. Gilpatrick and L. M. Jeffrey, *Trans. Amer. Geophys. Union*, 1956, **37**, 697.
[88] W. J. Ross and J. C. White, Oak Ridge National Laboratory, AEC Rept. ORNL-CF-57-2-37, 1957.
[89] E. M. Scadden and N. E. Ballou, *Analyt. Chem.*, 1953, **25**, 1602.
[90] U. Schindewolf, *Z. Elektrochem.*, 1958, **62**, 335.
[91] L. E. Scroggie and J. A. Dean, *Analyt. Chim. Acta*, 1959, **21**, 282.
[92] J. C. Sheppard, Hanford Laboratories Operation, AEC Rept. HW-51958, 1957.
[93] W. D. Shults, *et al.*, Oak Ridge National Laboratory, AEC Rept. ORNL-2776, 1959.
[94] E. L. Smith and J. E. Page, *J. Soc. Chem. Ind.*, 1948, **67**, 48.
[95] D. C. Stewart, Univ. of California Radiation Laboratory, AEC Rept. UCRL-585, 1950.

[96] D. C. Stewart and W. C. Bentley, *Science*, 1954, **120**, 50.
[97] M. Taube, *J. Inorg. Nuclear Chem.*, 1960, **15**, 171.
[98] K. Van Ipenburg, *Rec. Trav. Chim.*, 1961, **80**, 269.
[99] V. C. A. Vaughen and E. A. Mason, *Equilibrium Extraction Characteristics of Alkyl Amines and Nuclear Fuel Metals in Nitrate Systems.* ORNL Sub-contract No. 1327, Massachusetts Inst. of Technology, Summary Report 1958 to 1960, AEC Rept. TID-12665, Oct., 1960.
[100] C. Gerald Warren, *Solvent Extraction Studies.* Western State College of Colorado, TID-6150 Annual Report, 1960.
[101] *Idem, ibid.*, Western State College of Colorado, TID-11575, Monthly Progress Report, Jan. 1961.
[102] C. G. Warren and J. F. Suttle, *J. Inorg. Nuclear Chem.*, 1960, **12**, 335.
[103] Boyd Weaver, Oak Ridge National Laboratory, AEC Rept. ORNL-CF-60-7-108, p. 35, 1960.
[104] *Idem, ibid.*, AEC Rept. ORNL-CF-61-1-106, 1961.
[105] Boyd Weaver and D. E. Horner, *J. Chem. Eng. Data*, 1960, **5**, 260.
[106] J. M. White, P. Kelly and N. C. Li, *J. Inorg. Nuclear Chem.*, 1961, **16**, 337.
[107] *Idem, ibid.*, 1960, **14**, 225.
[108] A. S. Wilson, Proc. International Conference on Peaceful Uses of Atomic Energy, 1958, **17**, 348, P/544, U.N. Geneva.
[109] G. R. Wilson, Oak Ridge National Laboratory, AEC Rept. ORNL-2866, p. 82, 1960.
[110] R. S. Winchester, Los Alamos Scientific Laboratory, AEC Rept. LA-2170, 1957.
[111] R. P. Wischow and D. E. Horner, *Recovery of Strontium and Rare Earths from Purex Wastes by Solvent Extraction with D2EHPA.* Abstract 107, p. 38*M*, 138th Meeting A.C.S., New York, September, 1960.

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SHORT COMMUNICATIONS

The latent heat of fusion of ethylene carbonate

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DETERMINATIONS of latent heats of fusion by means of cooling curves, for example, by the method of Plato,[1] have the advantage that they do not entail separate determinations of heat capacities. The main field of application of such methods is in metallurgical research, *i.e.* in temperature ranges where heat capacities are difficult to determine, whereas in chemistry cooling curves are almost exclusively used for estimating the degree of purity of chemical substances.[2]

In the present investigation, the latent heat of fusion of ethylene carbonate has been determined by applying Plato's equation,

$$\frac{L_P}{L_Q} = \frac{V_{P,after}}{V_{P,before}} \times \frac{m_Q}{m_P} \times \frac{V_{Q,before}}{V_{Q,after}} \quad (1)$$

where L is the latent heat of fusion, m the mass, and V the rate of cooling (a complete theoretical treatment and derivation of equation (1) is given in the original paper by Plato). *p*-Toluidine was used as reference substance of known latent heat of fusion (L = 39·9 cals/g),[3] and of melting point comparable with that of ethylene carbonate. From the results obtained, the "thermodynamic" cryoscopic constant of ethylene carbonate has been calculated and is compared with K_{1000} values derived from freezing point measurements.

Experimental

Simple cooling curve apparatus was used for measuring the cooling curves. The bath liquid was liquid paraffin, and this was efficiently stirred in order to avoid any temperature gradients within the heat shield. An electrical heating coil was used.

The cryoscopic measurements were carried out in a modified Beckmann apparatus in which mechanical stirring was effected by an electrical make-and-break device.

Materials: The purification of ethylene carbonate has been described elsewhere.[4] The purified material used in this investigation had m.p. 36·2°, $n_D^{40°}$ 1·4199. *p*-Toluidine was purified by fractional distillation at reduced pressure to a m.p. of 44°. The solutes used for the cryoscopic measurements were of commercial grade, and were recrystallised before use.

Results and discussion

Typical cooling curves obtained for ethylene carbonate and for *p*-toluidine are shown in Fig. 1. They are based on temperature recordings at 1-min intervals. In Table I are summarised the rates of cooling, V_{before} and V_{after}, before and after solidification, and the values of the latent heat of fusion of ethylene carbonate calculated from these results, using equation (1).

TABLE I.—THE HEAT OF FUSION OF ETHYLENE CARBONATE

	Ethylene carbonate, 27·49 g		*p*-Toluidine, 20·29 g		L, *cal/g*
	V_{before}, °C/min	V_{after}, °C/min	V_{before}, °C/min	V_{after}, °C/min	
1	0·168	0·203	0·275	0·346	28·3
2	0·173	0·200	0·275	0·346	27·0
3	0·168	0·203	0·265	0·342	27·5
4	0·173	0·200	0·265	0·342	26·4

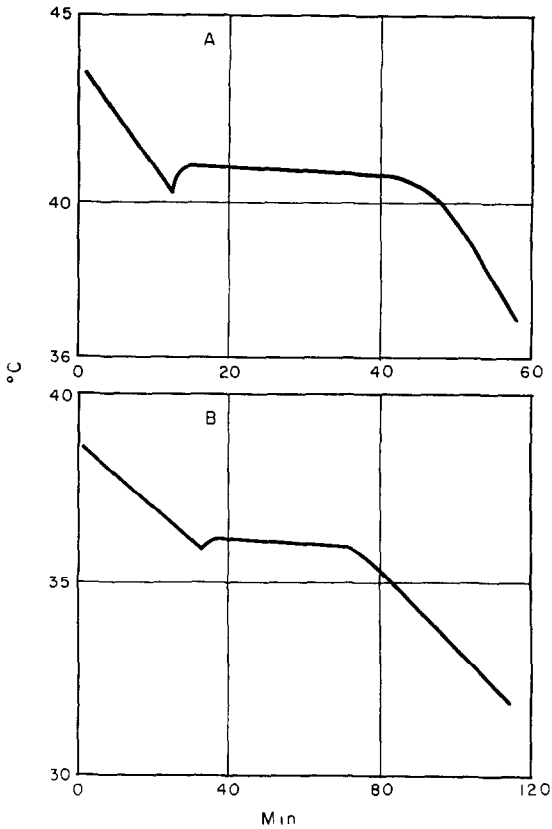


FIG. 1.—Cooling curves of *p*-toluidine (A) and of ethylene carbonate (B).

The mean value of L, 27·3 ± 0·6 cal/g, yields a "thermodynamic" cryoscopic constant of 6·96 ± 0·15°/mole. This value is in good agreement with the values of K_{1000} derived from the cryoscopic measurements, the results of which are given in Table II.

TABLE II.—THE CRYOSCOPIC CONSTANT OF ETHYLENE CARBONATE

Solute	Molal concentration	ΔT, °C	K_{1000}, °C/mole
Naphthalene	0·0221	0·154	6·95
	0·0258	0·177	6·87
	0·0359	0·250	6·96
	0·0362	0·254	7·03
p-Nitroaniline	0·0265	0·190	7·18
	0·0296	0·207	6·98
	0·0381	0·270	7·09
	0·0397	0·278	7·00
		Mean value:	7·01 ± 0·07

The value K_{1000} = 7·02 for ethylene carbonate was found independently by Gross and Schuerch.[5]

The present investigation shows that the method for determining latent heats of fusion from cooling curves, originally described by Plato, can successfully be applied to substances with melting points not far above room temperature. Although the accuracy is somewhat inferior to that attainable by the Nernst method, Plato's procedure has the advantage of requiring neither heat-capacity nor

heat-transfer data; furthermore, since only the rates of cooling before and after solidification are required for the evaluation of latent heats of fusion, complete cooling curves need not be recorded. The only requirement for the applicability of Plato's method is the availability of a comparison sample of known latent heat of fusion and of melting point close to that of the unknown substance, so that similar experimental conditions obtain for the measurements involved.

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Summary—The latent heat of fusion of ethylene carbonate, a useful cryoscopic solvent for many organic compounds, has been determined (*a*) from a study of its cooling curve, and (*b*) from cryoscopy. The results are shown to be in good agreement.

Zusammenfassung—Äthylencarbonat ist ein gutes kryoskopisches Lösemittel für viele organische Verbindungen. Seine latente Schmelzwärme wurde aus Abkühlungskurven und kryoskopischen Daten bestimmt. Die nach den beiden Methoden erhaltenen Werte stimmen gut überein.

Résumé—Les auteurs ont déterminé la chaleur latente de fusion du carbonate d'éthylene, solvent cryoscopique usuel pour de nombreux composés organiques: *a*) d'après une étude de sa courbe de congélation—*b*) par cryoscopie. Les résultats obtenus par les deux méthodes sont en bon accord.

REFERENCES

[1] W. Plato, *Z. phys. Chem.*, 1906, **55**, 721.
[2] W. P. White, *J. Phys. Chem.*, 1920, **24**, 393.
[3] *Int. Crit. Tables*, 1929, **5**, 133.
[4] R. F. Kempa and W. H. Lee, *J. Chem. Soc.*, 1958, 1936.
[5] S. K. Gross and C. Schuerch, *Analyt. Chem.*, 1956, **28**, 227.

Precipitation of copper salicylaldoximate from homogeneous solution

(*Received* 18 *September* 1961. *Accepted* 15 *October* 1961)

INTRODUCTION

IN 1930, Ephraim[1,2] proposed the use of salicylaldoxime as a reagent for the gravimetric determination of copper. An advantage of this organic reagent is its large solubility in the aqueous acidic solutions used for the precipitation of copper. Disadvantages are the tendency of the reagent to decompose and the formation of a gelatinous precipitate which is difficult to filter.

In the method to be described in this paper, a dense precipitate of copper salicylaldoximate is produced by reacting salicylaldehyde and hydroxylamine hydrochloride in the presence of copper^{II} ions.

EXPERIMENTAL

Reagents

Unless otherwise specified, all chemicals were reagent grade.

Copper solution: C.P. copper metal, 99·9% pure, J. T. Baker Chemical Co., Phillipsburg, New Jersey, U.S.A., was dissolved in nitric and sulphuric acids. The solution was standardised by electrolysis [43·01 mg of Cu/25 ml, standard deviation 0·09 mg (5 determinations)] and by precipitation with 8-hydroxyquinoline [43·19 mg of Cu/25 ml, standard deviation 0·17 mg (5 determinations)] by the method of Berg.[3]

8-Hydroxyquinoline: The Matheson Co., Inc., Norwood, Ohio, U.S.A.

Iron^{III} chloride: Harshaw Scientific, Cleveland 6, Ohio, U.S.A.

Nickel^{II} sulphate hexahydrate and hydroxylamine hydrochloride: J. T. Baker Chemical Co., Phillipsburg, New Jersey, U.S.A.

Salicylaldehyde: The Dow Chemical Co., Midland, Michigan, U.S.A.

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Salicylaldoxime: Eastman Organic Chemicals, Distillation Products Industries, Rochester 3, New York, U.S.A.

Procedure

Add a solution containing 0·65 g of salicylaldehyde in 250 ml of distilled water to approximately 25 ml of a weakly acidic solution containing 10–50 mg of copper. Adjust the pH to 2·9 by the addition of filtered 6*N* ammonium hydroxide or sodium hydroxide solution and cool in an ice bath to approximately 5°. Dissolve 0·33 g of hydroxylamine hydrochloride in 10 ml of distilled water and add 1 ml of this solution with stirring to the cold copper solution. When precipitation begins (approximately 15 min), add the remaining 9 ml of the hydroxylamine hydrochloride solution with stirring. Allow the mixture to stand overnight. Filter onto a glass fritted crucible, wash with cold distilled water, dry at 110° for 3 hr, and weigh as $Cu(C_7H_6O_2N)_2$; the conversion factor for $Cu/Cu(C_7H_6O_2N)_2$ is 0·1892.

Precipitation conditions

The concentration of the reagents, mode of addition, temperature of reaction, pH range for precipitation, *etc.*, were evaluated in preliminary investigations for the purpose of establishing a gravimetric method. The reaction of salicylaldehyde and hydroxylamine proceeded so rapidly at room temperature that it was found necessary to cool the solution of copper to approximately 5° in order to obtain a precipitate with desirable physical characteristics. Further, for complete precipitation of 50 mg of copper, 3 × the stoichiometric amount of salicylaldehyde and hydroxylamine had to be used. The addition of buffer was not found necessary, although the addition of the hydroxylamine hydrochloride solution lowered the pH from 2·9 to 2·6, where precipitation is still quantitative.[4]

Precipitates of copper salicylaldoximate were found to come to constant weight after drying for 3 hr at 110°.

In studies of the precipitation of copper in the presence of diverse ions, nickel^{II} was added as sulphate and iron^{III} was added as chloride.

RESULTS AND DISCUSSION

The results obtained by precipitation from homogeneous solution (PFHS) and conventional precipitation are shown in Table I. The values agree closely with those obtained by electrolysis, but not with precipitation with 8-hydroxyquinoline.

TABLE I.—DETERMINATION OF COPPER ALONE

Method of precipitation	Conventional	PFHS	
Copper taken, *mg* [a]	43·01	43·01	8·60
Copper found, *mg* *difference*	−0·32, ±0·00 −0·16, −0·25 +0·04, ±0·00	+0·11, +0·06 +0·06, +0·06 −0·23, +0·09	+0·01 +0·07
Standard deviation	±0·20	±0·13	

[a] Electrolysis value

TABLE II.—DETERMINATION OF COPPER IN PRESENCE OF NICKEL(^{II}) OR IRON(^{II})

Method of precipitation	Conventional	PFHS	Conventional	PFHS	
Diverse element	Ni^{2+}, 100 mg	Ni^{2+}, 100 mg	Fe^{3+}, 50 mg	Fe^{3+}, 100 mg	Fe^{3+}, 50 mg
Copper taken, *mg*	43·01	43·01	43·01	43·01	43·01
Copper found, *mg difference*	−0·08, +0·06	+0·15, +0·11	+0·13, +0·04	+0·43, +0·49	+0·15, +0·27

The determination of copper in the presence of diverse ions is shown in Table II. Both the conventional and the PFHS method gave satisfactory results with 100 mg of nickel^{II}. Separation from 100 mg of iron^{III} by PFHS was not satisfactory, but with 50 mg of iron^{III}, good results were obtained with both methods. However, filtration is easily accomplished when precipitation is carried out by PFHS; furthermore, reagent decomposition is avoided.

Acknowledgements—The authors acknowledge the partial assistance of the United States Atomic Energy Commission in supporting the investigation described herein under Contract AT(11-1)-582 and the help of Fred Kohl who performed some of the early exploratory work.

Summary—Salicylaldoxime can be synthesised in aqueous medium by the reaction of salicylaldehyde and hydroxylamine hydrochloride in order to precipitate copper in a readily filterable form. Copper can be easily separated from nickel^{II} and iron^{III}.

Zusammenfassung—Salizylaldoxim kann in wässriger Lösung synthetisiert werden durch Reaktion von Salizylaldehyd und Hydroxylaminhydrochloride um Kupfer in leicht filtrierbarer Form abzuscheiden. Kupfer kann derart leicht von Nickel und Eisen(II) getrennt werden.

Résumé—La salicylaldoxime peut être préparée synthétiquement en milieu aqueux par réaction de salicylaldéhyde et de chlorhydrate d'hydroxylamine afin de précipiter le cuivre sous forme facilement filtrable. Le cuivre peut être aisément séparé du nickel(II) et du fer(III).

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REFERENCES

[1] F. Ephraim, *Ber.*, 1930, **63**, 1928.
[2] *Idem., ibid.*, 1931, **64**, 1215.
[3] R. Berg, *Z. analyt. Chem.*, 1927, **70**, 341.
[4] L. P. Biefeld and D. E. Howe, *Ind. Eng. Chem., Analyt.*, 1939, **11** 251.

An investigation by electron-spin resonance of the redox indicator Variamine Blue

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VARIAMINE Blue [*N*-(*p*-methoxyphenyl)-*p*-phenylenediamine hydrochloride] is a redox indicator with many applications in analytical chemistry.[1] The redox potential at the colour change E_t, in the pH range 1·5–6·3, with reference to the standard hydrogen electrode, is given by the expression

$$E_t = +0{\cdot}712 - 0{\cdot}059 \text{ pH volt}$$

In this pH range the colourless Variamine Blue undergoes two-electron oxidation by strong oxidising agents (bromine, chlorine, *etc.*) to a violet-red iminoquinone.[2–4]

The colourless reduced form of Variamine Blue (R) combines reversibly with the violet-red iminoquinone (Q) to yield an intensely coloured blue quinhydrone (D).

$$R + Q \rightleftharpoons D$$

Polarographic investigation of Variamine Blue and its derivatives, and analysis of the potentiometric titration curves, have indicated[2–6] that the blue quinhydrone (D) may dissociate partially, in many cases, into a semiquinone-type ion (S) which has a free radical structure.

$$D \rightleftharpoons 2S^{\cdot}$$

Although the intense blue colour which appears during the colour change of Variamine Blue suggests that a dissociation of this type occurs, the potentiometric data cannot be taken in all cases as conclusive proof of such a dissociation. For example, Holden, Yager and Merrit[7] failed to detect paramagnetic resonance absorption in the closely related dyestuff, Bindschedler's Green, which on

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The determination of copper in the presence of diverse ions is shown in Table II. Both the conventional and the PFHS method gave satisfactory results with 100 mg of nickel^{II}. Separation from 100 mg of iron^{III} by PFHS was not satisfactory, but with 50 mg of iron^{III}, good results were obtained with both methods. However, filtration is easily accomplished when precipitation is carried out by PFHS; furthermore, reagent decomposition is avoided.

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the basis of potentiometric evidence[8] appears to dissociate in this manner. It was therefore thought desirable to investigate Variamine Blue by electron-spin resonance technique in order to clarify the mechanism of its oxidation.

EXPERIMENTAL

Solutions

(*i*) 0·01*M* *Variamine Blue base in benzene or carbon tetrachloride:* 250 mg of commercial Variamine Blue B hydrochloride dissolved in a little hot dilute hydrochloric acid was rendered strongly alkaline with 2*N* sodium hydroxide and the solution (containing precipitate) extracted with four 20-ml portions of benzene (or carbon tetrachloride). The benzene solution of the base was dried with sodium sulphate and diluted to 100 ml with benzene. This solution, which is stable for only a few days, was stored in the dark. It was standardised gravimetrically.

(*ii*) 0·01*M* *bromine in carbon tetrachloride:* This solution prepared from 0·026 ml of bromine in 100 ml of AnalaR carbon tetrachloride, was standardised iodometrically.

(*iii*) 0·01*M* *chlorine in carbon tetrachloride* was prepared by absorbing chlorine gas in carbon tetrachloride and was standardised iodometrically immediately before use.

Electron-spin resonance measurements

Electron-spin resonance measurements were made with a spectrometer operating at 9370 Mc/sec and a magnetic field modulated at 100 Kc/sec. The absorption signal, following amplification and phase-sensitive detection, was displayed on a pen recorder as the first derivative of the absorption curve. Relative radical concentrations were estimated by measurement of peak height on the first-derivative curve where the line shape remained unchanged. Absolute radical concentrations were estimated by an integration procedure using a solution of diphenyl picryl hydrazyl in benzene as standard. In some cases it was found convenient to use, for this purpose, previously standardised dextrose-charcoal samples.

Procedure: To 1·0-ml samples of 0·01*M* Variamine Blue solution in benzene (or carbon tetrachloride) different volumes of 0·01*M* bromine solution in carbon tetrachloride were added, and the solutions were made up to 3·0 ml with carbon tetrachloride. The mixtures were shaken vigorously and centrifuged, and the radical concentration was determined. The radical activity was confined to the precipitate.

RESULTS

The results of one series of experiments are shown in Fig. 1. The maximum radical concentration

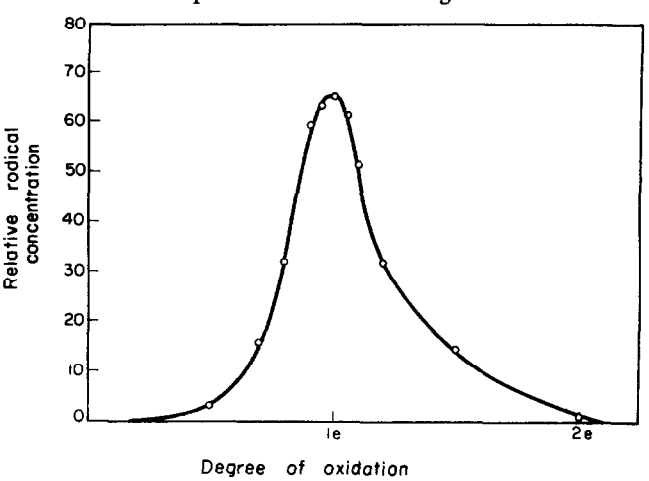


FIG. 1.—Effect of oxidation-state on the radical concentration in Variamine Blue-bromine solutions in carbon tetrachloride.

occurs at the one-electron oxidation stage. The precipitate obtained at the two-electron oxidation stage was inactive, but when mixed with the reduced Variamine Blue solution gradually developed an electron-spin resonance spectrum because of the reaction

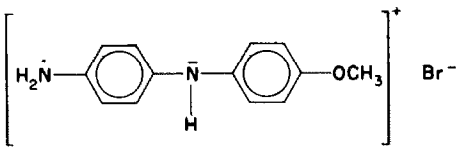
$$Q + R \rightleftharpoons D \rightleftharpoons 2S^{\cdot}.$$

Similar results were obtained when carbon tetrachloride or a mixture of carbon tetrachloride and benzene were used as solvents.

With chlorine as oxidising agent difficulty was found in centrifuging the precipitate on account of its density, but a similar variation of radical concentration with the degree of oxidation was observed. With chlorine the reaction was carried out in carbon tetrachloride only.

Magnetic results

The spectrum obtained with a Variamine Blue-bromine solution at the one-electron oxidation stage consists of a single narrow line. The g-factor of the radical is 2·003, close to the free-spin value, and the line-width (between peaks on the first-derivative curve) is 3·4 gauss. The absolute radical concentration in this solution corresponded to a dissociation to the free radical form (S·) of 25 ± 2%. The probable structure of the radical is:



Active precipitates obtained from benzene solutions were found to contain benzene of crystallisation.

Measurements in aqueous solutions

The radical-containing precipitate, when suspended in water, dissolved partially to give a blue-violet colour and the filtered solution gave a weak spectrum consisting of a single broad unresolved line. Quantitative measurements showed that the maximum radical concentration occurred between pH 2 and 3 (Fig. 2), corresponding to a dissociation to the free radical form of about 0·66%. The

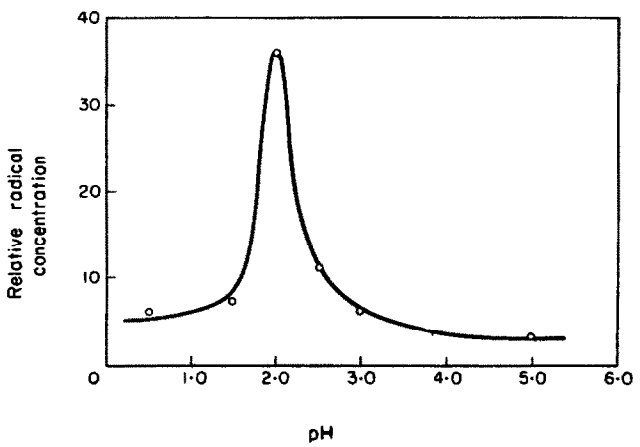


FIG. 2.—Effect of pH on the radical concentration in Variamine Blue-bromine solutions.

dissociation D ⇌ 2S· is therefore much less in water than in the solid state. Attempts to obtain a resolved spectrum for the radical in tetrahydrofuran and acetone were not successful. In the solid state the radical is stable for long periods.

These results are in accord with conclusions drawn from the potentiometric data and provide additional evidence for the view that in aqueous solutions of Variamine Blue, and especially in the pH range 2–3, significant dissociation to the free radical-ion form occurs. Similar results may be expected with other derivatives of Variamine Blue for which potentiometric data indicate dissociation to the radical form.

Acknowledgements—The authors thank Professor C. L. Wilson and Professor C. Kemball for their interest. One of us (L. E.) wishes also to thank The Queen's University of Belfast for a visiting Fellowship.

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Summary—A study of the redox indicator Variamine Blue by electron-spin resonance technique provided evidence for the free radical nature of the semi-quinone intermediate. When benzene solutions of the indicator are oxidised to the one-electron stage, deep-blue precipitates, showing strong electron-spin resonance absorption, are obtained. In aqueous solution dissociation to the free radical form is much less, with a pronounced maximum in the pH range 2 to 3.

Zusammenfassung—Eine Studie am Redoxindicator Veriaminblau mittels Elektronen-Spin-Resonanz zeigt Evidenz fur die Anwesenheit der semichinoiden Zwischenstufe als freies Radikal. Wenn benzolische Lösungen des Indicators zum Singelelektronderivativ oxydiert werden, erhält man einen tiefblauen Niederschlag, der starke Elektronenspinresonanz zeigt. In wässriger Lösung ist die Dissoziation zur freien Radikalform geringer. Ein Maximum besteht im pH-Bercich 2–3.

Résumé—Une étude du bleu de variamine, indicateur d'oxydo-réduction, par la méthode de résonance de l'électron-spin a montré la nature du radical libre de la semiquinone intermédiaire. Quand des solutions de l'indicateur dans le benzéne sont oxydées au premier stade: perte d'un électron, des précipités bleu fancé sont obtenus, montrant une forte absorption par résonance de l'électron-spin. En solution aqueuse, la dissociation an radical libre est beaucoup moindre, avec un maximum prononcé dans le domaine de pH 2 à 3.

REFERENCES

[1] L. Erdey, *Chemist-Analyst*, 1959, **48**, 106.
[2] É. Bányai, L. Erdey and F. Szabadváry, *Acta Chim. Acad. Sci. Hung.*, 1959, **20**, 307.
[3] É. Bányai and P. Zuman, *Coll. Czech. Chem. Comm.*, 1959, **24**, 522.
[4] L. Erdey, E. Zalay and E. Bodor, *Acta Chim. Acad. Sci. Hung.*, 1957, **12**, 251.
[5] L. Erdey, É. Bányai, E. Zalay and U. Tésy, *ibid.*, 1958, **15**, 65.
[6] L. Erdey, É. Bányai and É. B.-Gere, *Talanta*, 1959, **3**, 54.
[7] A. N. Holden, W. A. Yager and F. R. Merrit, *J. Chem. Phys.*, 1951, **19**, 1319.
[8] G. Schwarzenbach and L. Michaelis, *J. Amer. Chem. Soc.*, 1938, **60**, 1667.

Talanta, 1962, Vol. 9, pp. 333 to 335. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEW

Systematic Qualitative Analysis: An Introduction. G. A. MORRISON. Butterworth and Co. (Publishers) Ltd., London, 1961. pp. ix + 198. 25s.

THOUGH stated to be only an introduction, this book includes fifteen of the less common metals in an orderly concise scheme of semimicro qualitative inorganic analysis which can also be easily adapted for use in a more elementary form.

After a consideration of the factors involved in the formation of a precipitate (dissociation constants, buffered solutions and solubility constants), and of apparatus and techniques (an apparatus is shown which prepares H_2S in acetone when needed) there follows a full treatment of preliminary tests including a 10-page reference table showing the solubility of compounds of the more common metals in hot and cold water and in dilute and concentrated acids. One doubts, however, whether the latter is of much use at this stage of the analysis.

The theory of group separations is fully discussed, with useful tables of solubility products and pH conditions. The separation of cations follows one of the classical procedures, the alkaline earth metals being precipitated as carbonates (5th Group), although it is well known that significant losses of these ions occur in earlier groups. In an alternative procedure for separating strontium from calcium by the addition of potassium chromate in ammonia solution, the addition of ethanol to effect complete separation is omitted. Many will disagree with the author regarding the use of "spot tests", the only ones included being tests for Ag, Ni and Mg. In a treatise at this level one would wish for the inclusion of the more reliable spot reagents, especially for those cations, *e.g.* Sr, for which there is a dearth of other suitable confirmatory tests.

Running nomenclature diagrams are given for naming a precipitate or solution at any stage within a group separation. Those replace the usual tabular forms, but would appear to add to the difficulties in the interpretation of the instruction manual and in the writing up of the analysis.

Anions are identified by a number of separate investigations on different portions of the stock solution, and difficultly soluble substances are subjected to fusion, first with sodium carbonate and afterwards, if necessary, with sodium hydroxide.

The book, which is attractively produced, is a suitable "bench" handbook, and as it also contains basic theoretical principles, will be much welcomed by those who require a shorter text of advanced analysis.

W. F. JONES

Separation of the Heavy Metals. ANIL K. DE. Pergamon Press, Ltd., London, Paris, New York, 1961. pp. 308. 60s.

IN the last two decades, a large amount of work has been done on the separation of the heavy metals using modern techniques and a large volume of literature on the subject has been published in many different journals. It is pleasing to see a book which gathers together much of this material into a handy-sized volume.

The book deals with the liquid-liquid extraction and ion-exchange methods for the separation of the metals in the range $Z = 37$–102; the "intermediate heavy metals" have been included to cover most of the metals which are of some importance in the nuclear energy programmes. Some of the analytical techniques used to evaluate the separation techniques are given in a separate section, whilst a further section illustrates the roles of the techniques in some of the radiochemical separations used for processing spent reactor fuels.

The stated objective of the book is that of "bringing together and co-ordinating the enormous amount of literature made available during the last ten years" but the author only attempts "to include in this book a complete survey of the literature up to the middle of 1958." However some reviews, which appeared before 1958, are not included and since the author refers to two papers published in 1960, it seems that it should have been possible at least to list the titles of the many papers published in 1958–60.

The presentation of the theoretical aspects of liquid-liquid extraction is well done but the general description of the types of extraction is not so good; part of one of the diagrams is inverted, with the solvent boiler at the top of the diagram and a reflux condenser at the bottom, the author seems to have difficulty in deciding which of the apparatus shown has a fritted disc or a "small orifice" and some

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Systematic Qualitative Analysis: An Introduction. G. A. MORRISON. Butterworth and Co. (Publishers) Ltd., London, 1961. pp. ix + 198. 25s.

THOUGH stated to be only an introduction, this book includes fifteen of the less common metals in an orderly concise scheme of semimicro qualitative inorganic analysis which can also be easily adapted for use in a more elementary form.

After a consideration of the factors involved in the formation of a precipitate (dissociation constants, buffered solutions and solubility constants), and of apparatus and techniques (an apparatus is shown which prepares H_2S in acetone when needed) there follows a full treatment of preliminary tests including a 10-page reference table showing the solubility of compounds of the more common metals in hot and cold water and in dilute and concentrated acids. One doubts, however, whether the latter is of much use at this stage of the analysis.

The theory of group separations is fully discussed, with useful tables of solubility products and pH conditions. The separation of cations follows one of the classical procedures, the alkaline earth metals being precipitated as carbonates (5th Group), although it is well known that significant losses of these ions occur in earlier groups. In an alternative procedure for separating strontium from calcium by the addition of potassium chromate in ammonia solution, the addition of ethanol to effect complete separation is omitted. Many will disagree with the author regarding the use of "spot tests", the only ones included being tests for Ag, Ni and Mg. In a treatise at this level one would wish for the inclusion of the more reliable spot reagents, especially for those cations, *e.g.* Sr, for which there is a dearth of other suitable confirmatory tests.

Running nomenclature diagrams are given for naming a precipitate or solution at any stage within a group separation. Those replace the usual tabular forms, but would appear to add to the difficulties in the interpretation of the instruction manual and in the writing up of the analysis.

Anions are identified by a number of separate investigations on different portions of the stock solution, and difficultly soluble substances are subjected to fusion, first with sodium carbonate and afterwards, if necessary, with sodium hydroxide.

The book, which is attractively produced, is a suitable "bench" handbook, and as it also contains basic theoretical principles, will be much welcomed by those who require a shorter text of advanced analysis.

W. F. JONES

Separation of the Heavy Metals. ANIL K. DE. Pergamon Press, Ltd., London, Paris, New York, 1961. pp. 308. 60s.

IN the last two decades, a large amount of work has been done on the separation of the heavy metals using modern techniques and a large volume of literature on the subject has been published in many different journals. It is pleasing to see a book which gathers together much of this material into a handy-sized volume.

The book deals with the liquid-liquid extraction and ion-exchange methods for the separation of the metals in the range $Z = 37$–102; the "intermediate heavy metals" have been included to cover most of the metals which are of some importance in the nuclear energy programmes. Some of the analytical techniques used to evaluate the separation techniques are given in a separate section, whilst a further section illustrates the roles of the techniques in some of the radiochemical separations used for processing spent reactor fuels.

The stated objective of the book is that of "bringing together and co-ordinating the enormous amount of literature made available during the last ten years" but the author only attempts "to include in this book a complete survey of the literature up to the middle of 1958." However some reviews, which appeared before 1958, are not included and since the author refers to two papers published in 1960, it seems that it should have been possible at least to list the titles of the many papers published in 1958–60.

The presentation of the theoretical aspects of liquid-liquid extraction is well done but the general description of the types of extraction is not so good; part of one of the diagrams is inverted, with the solvent boiler at the top of the diagram and a reflux condenser at the bottom, the author seems to have difficulty in deciding which of the apparatus shown has a fritted disc or a "small orifice" and some

diagrams are awkwardly placed with respect to their descriptions, necessitating much page turning for reference from text to diagram.

The presentation of the corresponding part for ion-exchange is better but still has inadequate descriptions for some diagrams.

For each of the 30 or so metals listed, several methods of solvent extraction are described, but it becomes increasingly apparent that insufficient attention has been given to standardisation of the presentation. The percentage extraction (%E), is used in some methods, and an extraction coefficient (E, which is not defined in the theoretical section) is used in others; in yet further cases the amounts extracted are not denoted at all.

In some extraction methods the procedure for the determination of the metal is given, but in general no details are given correlating the "separated state" of the metal and the state used in its determination. In the case of indium, more comprehensive details for the extraction with oxine, including a list of interfering elements, are to be found in the analytical section than in the appropriate separation section. Tellurium is not mentioned in one of the three sections (liquid-liquid extraction.).

The best part of the book is the section concerned with radiochemical separations. In a brief but useful survey of existing methods, the author deals with such topics as the separation of radio-isotopes from target materials and the analysis of radioactive dusts.

In the lengthy appendix, which includes a comprehensive list of the characteristics of readily available ion-exchange materials and the physical constants of some organic solvents and chelating agents, the lack of correlation is again noticed: *n*-butyl phosphate is listed as such only in the appendix; in all extraction procedures it is called tri-butyl phosphate or TBP: the constants for dioxan—not listed in the extractions—are given, but those for some solvents such as tri-octylamine, used in some of the separations, are not given.

It would seem that in the promised future editions, due attention should be paid to these errors and to the correction of others such as "from such system," "procedures of heavy metals," "Gross Lanthanides have been separated," a comma at the end of a sentence; and to spelling mistakes such as Universitety (in the dedication), tungstan, volune, chunk (chuck) and the compound H_4O_3.

The uncommon type face and the brilliant white paper combine at first sight to give an impression of slightly blurred and uneven printing.

To summarise—this is excellent material somewhat spoiled by poor correlation and presentation of the various sections, but I look forward to a revised edition of this book, free from irritating errors.

L. S. BARK

Az analitikai Kémia módszereinek kialakulása (The Development of Methods of Analytical Chemistry). FERENC SZABADVÁRY. Akadémia Kiadó, Budapest, 1960. 418 pp. 100 Hungarian forint. In Hungarian.

This is the first work in the literature which deals with the history of analytical chemistry from ancient days up to the present time. The development of analytical chemistry is treated chronologically up to the end of the eighteenth century; separate chapters deal with the analytical works of ancient (1) and medieval (2) times, as well as of iatrochemistry (3), the phlogiston age (4), and from Lavoisier to Berzelius (5), while the works and life of Berzelius (6) conclude the first part of the book. In the following chapters the development of various branches of analytical chemistry is described separately; there are presented the further development of qualitative and gravimetric analysis (7), titrimetric analysis (8), organic analysis (9), electrogravimetry (10), optical methods (11), electrometric analysis (13) and other methods (14); in chapter 12 the development of theoretical analytical chemistry is presented. Subject and author indexes are also included.

The material has been collected mainly from original contemporary papers, and more than one thousand references are to be found. The book contains a number of citations from original texts. One hundred figures, mostly facsimiles, are reproduced in the book. If one merely looks through the illustrations, it is possible to get a good insight into the history of analytical chemistry. Analytical chemists of today will turn with interest to the pictures of the first gasometric device of Cavendish, the laboratory equipment of Lavoisier, the first atomic weights table of Berzelius, the title page of Fresenius' *Zeitschrift für analytische Chemie* which was the first journal of analytical chemistry (1862), the first spectroscope of Bunsen and Kirchoff, *etc.* There are a number of portraits of old and new analytical chemists. Short biographies of more than eight hundred scientists are presented, the most important being included in the text and references given for the others. Some details of the work of living analysts are mentioned.

The author is an analytical chemist himself and has published several original papers. He plans to publish the book in English and German, so that this very interesting text should soon be available to almost all analytical chemists in the world.

GYULA SVEHLA

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The author is an analytical chemist himself and has published several original papers. He plans to publish the book in English and German, so that this very interesting text should soon be available to almost all analytical chemists in the world.

GYULA SVEHLA

Chemical Indicators. É. BÁNYAI. Müszaki Könyvkiadó, Budapest, 1961. 361 pp. 31 Hungarian forint. In Hungarian.

THIS book, dealing with every type of chemical indicator, is divided into five chapters: a short historical introduction, acid-base indicators, redox indicators, precipitation indicators and complexometric indicators.

In the introductory part of each chapter the theory of the titrations is discussed *e.g.* acid-base reactions, some problems concerning oxidation-reduction, solubility and complex equilibria. Many examples in the text assist the reader to learn and apply the theory.

In the chapter on acid-base indicators, colour change, fluorescent, luminescent and other types of acid-base indicator are treated. A detailed review of their mechanism is given and the relevant data and physico-chemical constants for the most important indicators are summarised. This chapter also includes titration curves, indicator corrections, colorimetric measurement of pH, and many practical problems.

In the chapter on redox indicators, after the treatment of redox equilibria the author deals with colour-change redox indicators, the oxidation mechanism of redox indicators, the effect of pH, some problems of colour change, the rH exponent, *etc.* A very detailed table, with the most recent references, presents the physico-chemical constants of redox indicators, the change in oxidation potentials with change in pH, *etc.* The author also deals with the end-point detection of redox reactions in alkaline media and with chemiluminescent indicators.

Under the heading of precipitation indicators the mechanism of adsorption indicators is discussed, the recent theory of Schulek and Pungor being mentioned. An interesting part of this chapter is the use of redox and fluorescent adsorption indicators.

In the final chapter the author, on the basis of the most recent literature, discusses the mechanism of metal indicators, and the sensitivity, possibilities and limits of use of metal indicators. The application of luminescent and redox indicators for the end-point detection of chelometric titrations is mentioned. A table, showing all the important characteristics of metal indicators, is included.

The book will be useful for all who have problems concerning indicators. The theoretical part is so extensive that a very considerable knowledge of analytical chemistry can be acquired from it.

E. KÖRÖS

Talanta, 1962, Vol. 9, pp. 337 to 338. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

(Material for this section should be sent directly to the Associate Editor)

UNITED KINGDOM

Wednesday 28 *March* 1962: **Annual General Meeting** followed by **Short Lectures:** *Polarographic Society.* Physics Department, Imperial College of Science and Technology, Prince Consort Road, London, S.W. 7. 2.30 p.m.

Wednesday 4 *April* 1962: Meeting for reading of **Original Papers:** *Society for Analytical Chemistry* Burlington House, London, W.1. 7.00 p.m.

Thursday 5 *April* 1962: **Analytical Research:** Dr. J. HASLAM: *Royal Institute of Chemistry, Mid-Southern Counties Section* and *Portsmouth and District Chemical Society.* College of Technology, Portsmouth. 7.00 p.m.

Thursday 5 *April* 1962: **The Determination of Boron:** Dr. H. J. CLULEY and Dr. R. H. BIDDULPH: *Society for Analytical Chemistry, Midlands Section.* Wolverhampton and Staffordshire College of Technology, Wulfruna Street, Wolverhampton, 7.00 p.m.

Friday 6 *April* 1962: **The Assessment of Psychostimulants:** Discussion to be opened by Dr. M. W. PARKES: *Society for Analytical Chemistry, North of England Section* and *Biological Methods Group. Nag's Head Hotel,* Lloyd Street, Manchester. 7.15 p.m.

Monday–Friday 9–13 *April* 1962: **Feigl Anniversary Symposium:** *Society for Analytical Chemistry, Midlands Section,* under the patronage of *I.U.P.A.C.* University, Edgbaston, Birmingham 15 (see also *Talanta,* 1962, **9**, 185).

The following additions and minor alterations to the scientific programme have been made:

V. ANGER (Vienna, Austria)	*Bedeutung des Chemismus von organischen Farbreaktionen für bei analytische Forschung.*
A. BONDI (Jerusalem, Israel)	*Detection of Chemicals in Feeds.*
C. A. JOHNSON (Boots Pure Drug Co., Nottingham, U.K.)	*Tetrazolium Salts in Quantitative Colorimetric Analysis.*

Monday–Friday 9–13 *April* 1962: **Sixth Congress of the International Society for Fat Research:** *Society of Chemical Industry, Oils and Fats Group.* Imperial College of Science and Technology, Physics Building, Prince Consort Road, London, S.W.7.

The provisional list of papers to be presented includes:

Analytical Techniques

U. GLOOR (Basle)	*Quantitative Determination of Ubiquinones in Biological Material.*
A. HAUTFENNE (Brussels)	*The Estimation of Peroxides by Use of the Leuco-base of 2:6-Dichlorophenol-indophenol.*
K. DE JONG (Vlaardingen)	*Location of Double Bonds with Osmium Tetroxide.*
G. JURRIENS (Vlaardingen)	*Separation of Lipids with Poly-ethylene.*
H. K. MANGOLD and L. J. MORRIS (Austin)	*Utilisation of Modern Techniques in Studies of Unusual Seed Oils.*
R. MARCUSE (Gothenburg)	*Separation of Fatty Acid Carbonylic Derivatives by Thin Layer Chromatography.*
M. NAUDET (Marseille)	*The Location of Double Bonds in Unsaturated Fatty Acids.*
B. DE VRIES (Vlaardingen)	*Quantitative Separation of Cis- and Trans-Isomers by means of Complexes with Silver Ions.*

Spectroscopic Methods

D. CHAPMAN (Cambridge)	*High Resolution Nuclear Magnetic Resonance of Isomeric Glycerides.*
C. Y. HOPKINS and H. J. BERNSTEIN (Ottawa)	*Proton Magnetic Resonance and Fatty Acid Structure.*
L. J. MORRIS (London)	*Near Infrared Characteristics and Relative Polarities of Long-chain Hydroxy Compounds in relation to their Structures.*

L. A. O'NEILL and S. M. RYBICKA (Teddington)	*Some Applications of Chromatographic and Spectroscopic Techniques in Drying Oil Chemistry.*
J. ZAJIC (Prague)	*Application of Infrared Spectrophotometry to the Sacharose Esters.*

Physical Methods and Properties

E. FEDELI and A. ARPINO (Milan)	*Determination of Molecular Weights by Isothermal Distillation Technique—Applications in the Field of Rats.*
C. PAQUOT, R. PERRON and Mme. J. PETIT (Bellevue)	*Application of Differential Thermal Analysis to the Study of Lipids—II: Ternary Mixtures of 1-Mono-, 1:3- Di- and Tristearins.*
J. W. SELBY (Leatherhead)	*A Comparison of the Dilatometric and Calorimetric Methods for Determining the Solid Phase in Shortenings.*

Registration forms and further particulars may be obtained from Drs. F. BRADLEY and H. JASPERSON, Joint Hon. Secretaries, VIth Congress of the International Society for Fat Research, 14, Belgrave Square, London, S.W.1, England.

The **Annual General Meeting** of the *Scottish Section of the Society for Analytical Chemistry* was held on Friday 26 January 1962 at the *Grosvenor Restaurant*, Gordon Street, Glasgow. The Chairman, Mr. A. F. WILLIAMS, presided.

The following were elected Officers of the Section for the forthcoming year:

Chairman: Mr. A. F. WILLIAMS

Vice-Chairman: Dr. R. A. CHALMERS

Hon. Secretary and Treasurer: Mr. J. BROOKS, Research and Development Department, I.C.I. Ltd., Nobel Division, Stevenston, Ayrshire.

UNITED STATES OF AMERICA

Thursday 15 *March* 1962: **An Automatic Approach to the Microdetermination of Carbon and Hydrogen:** Dr. H. F. HABER: *Metropolitan Microchemical Society.* (see also *Talanta*, 1962, **9**, 186).

Tuesday 3 *April* 1962: **Atomic Absorption Spectroscopy:** Mr. DAVID MANNING and Mr. WALTER SLAVIN: *Society for Applied Chemistry, New York Section.* Statler-Hilton Hotel, New York, N.Y. 8.00 p.m.

Wednesday–Friday 13–15 *June* 1962: **Analytical Automation and Data Processing:** *Annual Summer Symposium* of *Division of Analytical Chemistry, American Chemical Society* and *Analytical Chemistry.* College Park, Maryland (see also *Talanta*, 1962, **9**, 186).

The following minor alterations to the scientific programme have been made:

H. FREUND	*Graduate Instruction Involving Continuous Automation Systems.*
A. SAVITZKY and M. J. E. GOLAY	*Some Numerical Operations on Analytical Data.*
R. E. WAINERDI, D. GIBBONS and L. E. FITE	*Automation of Radioactivation Analytical Method, including Computer Data Processing.*
W. J. BLAEDEL and G. P. HICKS	*Automatic Enzyme Procedures.*

The Officers for the current year of the *Division of Analytical Chemistry, American Chemical Society* are:

Chairman: Mr. JOHN MITCHELL, JR.

Chairman-elect: Dr. L. B. ROGERS

Secretary-Treasurer: Dr. DONALD H. WILKINS, General Electric Research Laboratory, Schenectady, N.Y.

Talanta, 1962, Vol. 9, p. 339. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Ultraviolet spectrophotometric determination of scandium with Tiron: HIROSHI HAMAGUCHI, NAOKI ONUMA, ROKURO KURODA and RYUITIRO SUGISITA. (1 *January* 1962).

Stepwise determination of cadmium, mercury and tellurium: K. L. CHENG. (1 *January* 1962)

Ion exchange in mixed solvents: Adsorption behaviour of uranium and thorium on strong base anion-exchange resins from mineral acid-alcohol media: Separation methods for uranium and thorium: J. KORKISCH and G. E. JANAUER. (1 *January* 1962).

A polarographic study of dissolved oxygen—II: V. S. GRIFFITHS and M. I. JACKMAN. (8 *January* 1962).

The determination of the oxidation states of tracer uranium, neptunium and plutonium in aqueous media: S. C. FOTI and E. C. FREILING. (8 *January* 1962).

The application of an improved steam distillation apparatus to the determination of fluorine in rocks and minerals: C. O. INGAMELLS. (12 *January* 1962).

The determination of nitrite ion in the presence of large quantities of azide ion: H. F. COMBS and E. L. GROVE. (13 *January* 1962).

Semimicro iodometric determination of thallium^{III} by an amperometric method with two polarisable electrodes: RITA BHATNAGAR, M. L. BHATNAGAR and N. K. MATHUR. (15 *January* 1962).

Phase titrations—I: Binary systems involving carbon tetrachloride and binary systems involving carbon disulphide: D. W. ROGERS and ROBERT KOLEJ. (17 *January* 1961).

The effect of some anions on the spectrophotometric absorption of bis (di-n-octylethylenediamine) Cu^{II} complexes in Hexone: D. BETTERIDGE and T. S. WEST. (18 *January* 1962).

The continuous determination of uranium in impure solutions by gamma spectrometry: M. R. HAYES and A. P. SEYFANG. (22 *January* 1962).

Spot test for 2- and 4-valent sulphur in organic compounds based on reduction with Raney alloy: FRITZ FEIGL and DORA HAGUENAUER-CASTRO. (25 *January* 1962).

Spot test for bivalent sulphur based on pyrolysis with mercuric cyanide: FRITZ FEIGL and E. LIBERGOTT. (25 *January* 1962).

Talanta, 1962, Vol. 9, pp. 341 to 348. Pergamon Press Ltd. Printed in Northern Ireland

DIE BESTIMMUNG KLEINER FLUORMENGEN—II

DIE BESTIMMUNG VON FLUOR MIT ZR-ERIOCHROMCYANIN-LACK OHNE VORHERIGE ABTRENNUNG IN STARK MINERALISIERTEN WÄSSERN

ROMAN VALACH
Geologische Zentralanstalt, Prag, Tschechoslowakei

(*Received* 5 *September* 1961. *Accepted* 20 *November* 1961)

Zusammenfassung—Es wird eine hochempfindliche spektrophotometrische und photometrische Bestimmung von Fluor beschrieben, welche auf der Entfärbung des Zirkonium-Erichromcyanin-Lackes in 0,2 n Salzsäure beruht. Der Störeffekt eines großen Sulfatüberschusses wird auch bei hohen Bikarbonat- oder Kieselsäure-Gehalten durch Fällung von Bariumsulfat aus der schwachsaueren Lösung von sehr niedriger Fluorkonzentration ausgeschaltet, wo die Mitfällung von Bariumfluorid nicht eintritt. Das Fluoaluminat wird durch Alkalisieren zerlegt. Die Bildung einer störenden Eisen(III)-Eriochromcyanin-Verbindung wird durch Abwarten der Abscheidung von Eisenhydroxyd nach Entweichen des Kohlendioxyds verhindert.

Aus der kritischen Übersicht der Bestimmungen von Fluor[1] folgt, daß die Bestimmung von kleinen Fluor-Totalkonzentrationen nach der meistens zeitraubenden Abtrennung von ihrer Begleitkomponenten nur selten prinzipielle Vorteile hat. Der Autor widmete deshalb der Zr-Eriochromcyanin-Methode seine Aufmerksamkeit, da sich bei ihr nach Literaturangaben Störungen durch anwesende Kationen und Anionen am wenigsten bemerkbar machen und modifizierte sie so, daß auch bei Analysen von stark mineralisierten Wässern keine besondere Fluor-Abtrennung vorausgehen muß.

Nach experimentell nicht bewiesenen Angaben[3,4] kann man Sulfate, welche bei Fluor-Analysen von höher mineralisierten Wässern meistens die größten Fehler verursachen, als Bariumsulfat abtrennen, obwohl derselbe Niederschlag auch als Kollektor des wenig löslichen Bariumfluorids dient.[5] In der vorliegenden Arbeit wird deshalb vor allem die Beseitigung der durch Sulfate bewirkten Störung beschrieben.

EXPERIMENTELLER TEIL

Die Messungen wurden mit Hilfe des Spektrophotometers Uvispek der Firma Hilger mit Wolfram-Glühbirne und Glasprisma (Spaltbreite 0,1 mm) und mit Hilfe des Photometers Spekker derselben Firma (Filter 520 und 550 mμ) in Glasküvetten mit 4 cm Meßlänge (wenn nichts anderes angeführt ist) durchgeführt.

Die Stammlösung von 0,100 mg F^-/ml wurde durch Auflösen von 0,2210 g Natriumfluorid (p.a. Merck) in 1000 ml dest. Wasser zubereitet und in einer paraffinierten Flasche aufbewahrt. Durch Verdünnen der Stammlösung im Verhältnis 1 + 19 wurde die Eichlösung von 5 μg F^-/ml hergestellt.

Die Eriochromcyanin-Lösung (im weiteren Text verkürzt ECC) wurde durch Auflösen von 1,20 g ECC (Merck) in 1000 ml dest. Wasser zubereitet. Zur Stabilisierung wurde mit 1 ml konz. chlorfreier Salzsäure angesäuert, und zum Schutz vor Verschimmelung wurde Quecksilberjodid bis zur Sättigung zugegeben.

Die Zirkonium-Lösung wurde durch Auflösen von 0,160 g $ZrOCl_2 \cdot 8H_2O$ in ungefähr 40 ml dest. Wasser zubereitet, anschließend in verdünnte, ausgekühlte Salzsäure (500 ml konz. chlorfreie HCl + ca. 400 ml H_2O) gegossen und auf 1000 ml aufgefüllt. In dieser Lösung besteht bei Zimmertemperatur keine Gefahr der Polymerisation der Zirkonium-Ionen. Wenn die Zirkonium-Lösung aus Zirkoniumnitrat zubereitet wird, ist es notwendig, die entsprechende Menge in Chlorid überzuführen, ohne daß sich nach dem Abdampfen der Stickoxyde infolge zu hoher Temperatur das in der Salzsäure unlösliche Zirkoniumoxyd bildet.

Die Zr-ECC-Lösung wurde durch Pipettieren der Zr-Lösung in einen Trichter mit kleiner Ausgangsöffnung, aus welcher sie langsam in dasselbe Volumen einer vollkommen gemischten ECC-Lösung zuläuft, hergestellt. Sie ist nach 24–30 St. gebrauchsfähig. Die Hydroxyd-Lösung wurde durch Auflösen von 19,0 g KOH in 50 ml Lösungsvolumen zubereitet.

RESULTATE

Allgemeine Ergebnisse

Die erhaltenen Absorptionsspektren von ECC und Zr-ECC bei ECC-Überschuß stimmen mit den Angaben der Literatur[2,3] überein. Die Absorptionskurve des Lackes ist jedoch in diesem Fall durch den Überschuß des freien Farbstoffes, welcher nach der Zersetzung von Zr-ECC durch die Fluoride noch wächst, verwischt. Aus der Figur 1, in welcher auch die Spektren des Lackes bei Zirkonium-Überschuß

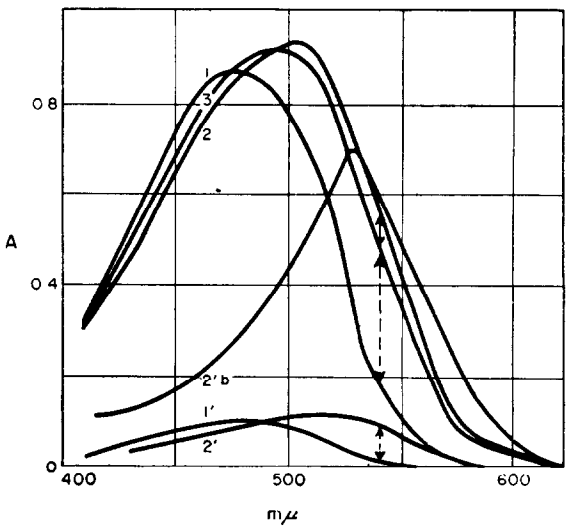


FIG. 1. Absorptionsspektrum von ECC und Zr-ECC in 0,2 n HCl

1. 90 μmol ECC,
2. 90 μmol ECC + 18 μmol Zr^{IV},
3. 90 μmol ECC + 18 μmol Zr^{IV} + 4,8 μmol F^-,

1'. 9 μmol ECC
2'.9 μmol ECC + 18 μmol Zr^{IV},
2'b. 9 μmol ECC + 180 μmol Zr^{IV}.

Photometriert in Küvetten von 1 cm Meßlänge. Weitere Angaben sind aus der Arbeitsvorschrift ersichtlich.

enthalten sind, ist ersichtlich, daß die Wellenlänge des Absorptions-Maximums von Zr-ECC bei 530 mμ und die des größten Unterschiedes in der Färbung des Farbstoffes und seines Lackes und des größten Entfärbungseffektes der Fluoride bei 540 mμ liegt. Thatcher[3] fand bei zwei verschiedenen ECC Präparaten bei 520 bzw. 540 mμ die größte Einwirkung der Fluoride.

In 0,1 n Salzsäure beträgt nach Megregian[2] das molare Verhältnis von Zr:ECC im Lack 1:3, bei höherer Azidität ist dieses Verhältnis wahrscheinlich infolge der Dissoziation des Lackes verwischt. In 0,2 n Salzsäure zersetzen 4,8 mμ F^-, wenn man nach dem Verlauf der Absorptionskurven urteilt, eine ungefähr 5,5 mμ gebundenem Zirkonium entsprechende Menge an Lack. Das Reaktionsverhältnis von F:Zr ist also unter diesen Bedingungen ungefähr 1:1. Diese Tatsache stimmt damit

überein, daß das Ion ZrF^{3+} das stabilste System von Fluor und Zirkonium ist,[6] und erklärt die hohe Empfindlichkeit der Zr-ECC-Methode.

Die Neigung der Eichkurve ändert sich schon bei relativ kleinen Temperaturunterschieden der photometrierten Lösungen (siehe Figur 2) und beim Gebrauch verschiedener Zr-ECC-Lösungen, auch wenn sie auf dieselbe Weise aus demselben Präparat zubereitet wurden. Die Wahl des Bezugspunktes der Eichkurve und die Art der Bestimmung deren Verlaufes beeinflußt infolge der erwähnten Umstände markant die Reproduzierbarkeit der analytischen Resultate. Die meisten Autoren,[2,3,7,8] welche die vorliegende Methode verbesserten, bestimmten deshalb den Bezugspunkt und die Eichkurve anders.

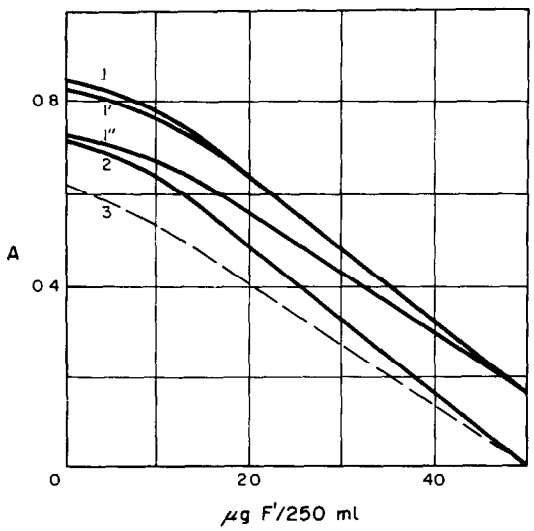


FIG. 2. Eichkurven von Fluor in 0,2 n Säure

1. HCl + $HClO_4$ (1,5 + 1),
2. HCl, gemessen gegen 50 μg F 250 ml in 0,2 n HCl,
3. HCl + 15 mg Triäthanolamin in 250 ml, photometriert gegen eine auf gleiche Weise zubereitete Lösung von 50 μg F, Messungen bei 21°,

1′, 1″, Messungen bei 24° und 31°. Sonstige Daten wie bei 1. Die weiteren Angaben sind aus der Arbeitsvorschrift ersichtlich.

Die Genauigkeit der Bestimmungen von Fluor in den Proben wird am wenigstens beeinflußt, wenn man eine Standardlösung von Fluor, deren Fluorgehalt einem passenden Punkt am Ende des linearen Verlaufes der Eichkurve entspricht, als Bezugslösung wählt, und wenn man die Resultate berücksichtigt, welche beim Studium des Störeffektes der Sulfate festgestellt wurden. Diesen Ansprüchen entspricht am besten eine Lösung mit 50 μg F/250 ml. Weiter ist es notwendig, bei jeder Serie von Bestimmungen die Neigung der Eichkurve mit einigen weiteren Standardlösungen nachzuprüfen und bei der Zugabe von Zr-ECC zur Analysenlösung gründlich zu mischen.

Die Extinktionswerte verschiedener Anteile einer 25 μg F/250 ml Standardlösung, welche in erwähnter Weise photometriert wurden, variierten meistens um ±0,010, d.h. um ±3%.

Genügend stabil wird die Farbintensität der Lösungen eine halbe Stunde nach der Vereinigung der Reaktanten.

Die Empfindlichkeit der Zr-ECC-Methode ist nach der unten angegebenen Arbeitsvorschrift annähernd 7 × größer als in der ursprünglichen Modifikation.[2] Bei Benutzung des Photometers Spekker wird sie um ungefähr $\frac{1}{3}$ vermindert.

Störeffekt der Sulfate, Bikarbonate und Kieselsäure

Aus Tabelle 1 ist ersichtlich, daß bei der Fällung der Sulfate aus neutralem Milieu Fluorverluste entstehen, welche mit wachsender Fluor-Konzentration steil und mit wachsendem Sulfatüberschuß mäßig ansteigen. Die Verluste lassen sich auch durch Fällen des Bariumsulfates aus 1 %igen Lösungen von Kaliumnitrat nicht vermindern, obwohl beide Ionen dieses Salzes vom Niederschlag leicht adsorbiert werden.[9] Man muß deshalb annehmen, daß die beobachteten Verluste hauptsächlich durch Mitfällung des wenig löslichen Bariumfluorides mit dem Bariumsulfat verursacht werden.

TABELLE 1.—DER EINFLUß DER F^-– UND SO_4^{2-}–KONZENTRATION AUF DIE FLUORVERLUSTE BEIM FÄLLEN DES BARIUMSULFATES AUS NEUTRALEM MILIEU

gegeben in 100 ml		%-Fehler der gefundenen Fluormenge	Gewichtsverhältnis SO_4^{2-}/F^-		%-Fehler · 10^{-3} SO_4^{2-}/F^-	
F^-, μg	SO_4^{2-}, mg					
12	2	0	165		0	
12	20	+ 8		1650		+5
20	2	−15	100		−150	
20	40	−37		2000		−18
90	2	−11	22		−500	
90	40	−50		450		−110

Die oben angedeutete Modifikation der Zr-ECC-Methode wurde so ausgearbeitet, daß man das Fluor mit vollkommen genügender Empfindlichkeit in Lösungen bestimmen kann, in welchen bei der Fällung von Bariumsulfat keine Fluorverluste entstehen.

Obwohl in neutralen Lösungen von Natriumfluorid und Natriumsulfat bis zur Konzentration von ungefähr 50 μg F/250 ml das Fluor-Ion mit dem Bariumsulfat nicht mitgefällt wird, traten in Lösungen, welche dieselbe Fluorkonzentration enthalten, Verluste ein, wenn in ihnen Bikarbonate neutralisiert wurden, wie sie der Zusammensetzung starker Bikarbonat-Mineralwässer entsprechen. Die Verluste kann man durch Fällen des Bariumsulfates aus sauerer Lösung vermeiden. Infolge des erhöhten Dampfdruckes von Fluorwasserstoff, in dessen Form das Fluor bei niedrigen Konzentrationen vorwiegend flüchtig ist,[10] und der höheren Löslichkeit des Bariumsulfates im saueren Milieu (z.B. werden in 0,02 n HCl 7 mg $BaSO_4$/l. gelöst[9]), ist es aber notwendig, die Azidität der Lösung, aus der Sulfat in der Nähe desSi edepunktes gefällt wird, möglichst niedrig zu erhalten.

Zu diesem Zweck war eine Lösung von ungefähr 0,02 n Salzsäure und 0,02 n Bariumchlorid am geeignetsten. Da aber kleine Sulfatmengen unter diesen Bedingungen so langsam gefällt werden, daß positive Fehler entstehen, ist es notwendig, den Sulfatgehalt vor der Fällung auf mindestens 20 mg in 200 ml zu erhöhen.

Bei der Neutralisation einer Lösung von 20 μg F und 350 mg Bikarbonaten in 250 ml mit Salzsäure, welche 200 mg Chloride enthielt, erhöhte sich der gefundene Fluorgehalt je nach der Qualität der Säure um 5–10 %. Diese Verschiebung des Resultates entsteht dadurch, daß die Chloride mit Zirkonium[6] oder sogar mit Zirkonyl

(siehe Fig. 2) schwache Komplexe bilden, und daß in der verwendeten Salzsäure wechselnde Spuren von Flußsäure enthalten sind. Ersatz der Salzsäure durch Perchlorsäure, von der keine Komplexe mit Zirkonium bekannt sind, bewährte sich nicht, weil wahrscheinlich der Störeffekt des unvollständig gefällten Sulfates in Perchlorsäure durch das Fehlen der Konkurrenz der Chlorionen größer ist.

Für ausnahmsweise vorkommende Bikarbonatüberschüsse von 4 und mehr Größenordnungen ist es also notwendig, mit Hilfe von fluorfreien Bikarbonat-Präparaten Korrekturnomogramme zur Eliminierung des Einflusses der gebrauchten Salzsäure zu ermitteln. Ein einfacher Korrekturfaktor ist unbrauchbar, da der Einfluß der Chloride mit sinkendem Fluorgehalt anwächst.

Das direkte Ansäuern einer Lösung von 1 mg F^- und 50 mg SiO_3^{2-}/l. verursacht keine größeren Fehler (−5%) der Fluorbestimmung. Wenn aber in einer solchen Lösung nach dem Verdünnen Sulfat ausgefällt wird, können prinzipielle Fehler entstehen, welche mit Vergrößerung des Sulfatgehaltes anwachsen. Diese ziemlich variablen Fehler betrugen bei 2000-fachen Sulfatüberschuß gegenüber den Fluoriden bis zu −36%. Verursacht wurden sie wahrscheinlich durch Mitreißen des im sauren Milieu entstandenen Kieselsäure-Gels mit daran adsorbierten Fluoriden durch den Bariumsulfatniederschlag. Verhindern kann man sie dadurch, daß man die Lösungen, bevor sie angesäuert werden, verdünnt und einige Stunden erwärmt, wodurch das Fluosilikat wahrscheinlich zersetzt wird.

Störeffekte der Aluminium- und Eisen/III/*-Ionen und der Phosphate*

Die Beseitigung des Störeffektes von Aluminiumionen wurde durch Analysen von Lösungen verfolgt, in welchen das Aluminium mit Fluor wenigstens 3 Tage bei pH 3–5 reagieren konnte. In Lösungen vom pH 2, denen die Aluminium-Ionen erst knapp vor der Analyse oder sogar erst nach der Beimischung des ausgenützten Chelates[11] zugesetzt wurden, konnte man nämlich beobachten, daß der verursachte Störeffekt mit der Zeit wächst. Am besten gelang es, die Fluoaluminate auch bei genügend großem Aluminiumüberschuß nach Fällung der Sulfate bei einem pH-Wert von annähernd 13 zu zerlegen. Unter den Bedingungen der photometrischen Bestimmung (pH 1) kommt es dann nicht mehr zu ihrer Rekombination. Näheres ist aus der Arbeitsvorschrift ersichtlich.

Größere Mengen von Eisen(III)-Ionen, welche bei dem vorgeschlagenen Verfahren vor allem beim Alkalisieren aus den gegebenenfalls enthaltenen Eisen(II)-Bikarbonaten entstehen, bilden mit ECC ein ähnlich gefärbtes Chelat wie Zirkonium. Negative Fehler, welche auf diese Weise auch bei einem Nullgehalt an Fluor entstehen, kann man am besten verhindern, indem man die Abscheidung von Eisen(III)-Hydroxyd nach Entweichen des Kohlendioxydes abwartet. Das Fluorid wird von dem langsam entstehenden Niederschlag nach fremder[12] und eigener Erfahrung nicht adsorbiert.

Von den Reagenzien, welche zur Tarnung oder Reduktion der Eisen/III/-Ionen benutzt werden, hat sich Triäthanolamin am besten bewährt. Da es aber die Neigung der Eichkurve bzw. die Empfindlichkeit der Bestimmung von Fluor (siehe Fig. 2) infolge der Bildung schwacher Zirkoniumkomplexe verringert und noch weitere Komplikationen verursacht, ist es besser, das oben angegebene Verfahren zu gebrauchen.

Die in Wässern meistens in kleineren Mengen als die Fluoride enthaltenen Phosphate stören die Fluorbestimmung weniger bei niedriger Temperatur und in saurer

Lösung,[3] vor allem von Salzsäure. Der Störeffekt der Phosphate wird deshalb durch Kühlen und Ansäuern der Lösung vor Zugabe des Zr-ECC vermindert. Aber auch nach dem Ansäuern ist es notwendig, die sauere Zr-ECC-Lösung gleich zuzugeben, damit die in der vorgeschlagenen Modifikation höchstmögliche Konzentration an Wasserstoff-Ionen in der Lösung bald erzielt wird. Bei diesem Verfahren besteht auch nicht die Gefahr der Rekombination der Fluoaluminate.

TABELLE 2. EINFLUß EINER REIHE VON KOMPONENTEN AUF DIE BESTIMMUNG DES FLUOR-GESAMTGEHALTES

gegeben 1 mg F/l. und mg/l. von				gefunden mg F/1.
4000 SO_4^{2-},	3500 HCO_3,	2500 K^+,	1300 Na^+	1,05
4000 SO_4^{2-},	1000 Ca^{2+}, 1200 Cl^-,	200 K^+,	1300 Na^+	1,04
4000 SO_4^{2-},	100 SiO_3^{2-}			0,95
1000 SO_4^{2-},	4 Al^{3+}			1,03
40 Fe^{2+},	1500 HCO_3^-		sat. CO_2	0,96
	analysiert 1 Woche nach der Zubereitung			
1,3 PO_4^{3-}		1,05	2 $B_4O_7^{2-}$	1,02
2,6 PO_4^{3-}		1,14	50 NO_3^-	1,04
5,2 PO_4^{3-}		1,60	8 Al^{3+}	0,96
2 AsO_4^{3-}		1,02	2 Mn^{2+}	1,02
10 AsO_4^{3-}		1,22	2,Be^{2+}	1,00

Die Bestimmungen wurden auf der Grundlage der im Text folgenden Arbeitsvorschrift nach Ansäuern ungefähr 18° warmer alkalischer Lösungen durchgeführt.

ARBEITSVORSCHRIFT

Nach dem Absetzen des Eisenhydroxydes pipettiert man aus den klaren Anteilen der hoch mineralisierten Wässer ein entsprechendes Volumen (z.B. aus einer Lösung von ca. 1 mg F/l. 25 ml). Dieses verdünnt man auf 200 ml und erwärmt es 3 h bei 40° bzw. läßt es nach Erwärmen über Nacht stehen. Der Sulfatgehalt der Probe wird mit einer Natriumsulfatlösung auf mindestens 20 mg in 200 ml eingestellt. Nach Aufkochen wird die Lösung mit 0,5 n Salzsäure neutralisiert und mit 3,0 ml überschüssiger Säure versetzt. Sulfat wird unter ständigem Rühren mit 25 ml einer 2%-igen saueren (5 ml konz. HCl/1) Bariumchloridlösung gefällt, die Lösungen zum Sieden gebracht, ungefähr 8 h auf 60° erwärmt und nach Auskühlen in einem 250 ml Meßkolben zur Marke aufgefüllt und gemischt.

24–48 h nach der Fällung werden 20 ml der klaren Lösung in ein 50 ml Becherglas pipettiert, mit 0,25 ml Kaliumhydroxyd-Lösung versetzt (mit Hilfe einer 1 ml Bürette) und 1 h auf 40° erwärmt. Anschließend werden bei elektromagnetischer Mischung schnell 0,25 ml konz. Salzsäure und 1,5 ml Zr-ECC-Lösung zugegeben. Hierbei muß—vor allem bei erhöhter Phosphat-Konzentration—stark gekühlt werden.

Nach 45–75 min wird die Lösung in Küvetten von 4 cm Meßlänge gefüllt und bei 540 mμ gegenüber einer gleich verarbeiteten Eichlösung von 50 μg F/250 ml photometriert. Die Resultate wertet man mit Hilfe einer Eichkurve aus, deren Verlauf man während jeder Bestimmungsserie mittels vier weiterer Eichlösungen nachprüft.

Während 8 Arbeitsstunden, welche meistens über 3 Tage verteilt sind, kann man ungefähr 15 Bestimmungen durchführen. Das vorgeschlagene Verfahren ist deshalb

bei einer größeren Anzahl von Bestimmungen zeitsparender als die Bestimmung von Fluor mit ECC in stark mineralisierten Wässern nach vorangehender Abtrennung.[2]

Bei ungefähr 200 analysierten Proben von stark mineralisierten Wässern (Rückstand 5 bis 20 g/l.) schwankten die Resultate relativ um ± 5 bis 10%, was bei einem Gehalt von 2 mg F/l. etwa ± 1 bis $2 \cdot 10^{-3}$% F im Rückstand entspricht, was vollkommen hinreichend ist.

Im Vergleich mit einer großen Reihe von Methoden, von welchen nur die vor kurzem veröffentlichte Anwendung von Lanthan-Chloranilat[13] angeführt sei (bei der Sulfate, Chloride und Nitrate bis zum sechsmaligen Überschuß nicht stören und alle Kationen mit Ausnahme von Amonium-Ionen stören) ist das vorgeschlagene Verfahren also wesentlich besser. Auch im Bezug zu den älteren Modifikation- der Zr-Eriochromcyanin-Methode, die schon in der ursprünglichen Form von Megregian[2] die oft als Standardmethode[14,15] gebrauchte Bestimmung mittels Zr-Alisarin übertraf und ebenfalls von dem erwähnten Autor gründlich untersucht wurde,[16] ist das vorgeschlagene Verfahren vorteilhafter, da es eine einfachere und schnellere Bestimmung von Fluor (ohne Destillation) in relativ kompliziertem Material ermöglicht. Die erwähnten Vorteile, zu welchen auch die hohe Bestimmungsempfindlichkeit zählt, sind jedoch immer noch nicht so groß, daß ein weiteres intensives Ausfinden noch schnellerer Bestimmungsweisen für dieses physiologisch sehr aktive und ind der Erdrinde verhältnißmäsig reichlich enthaltene Element nutzlos werden dürfte.

Die vorliegende Studie weist wahrscheinlich auch auf die Grenzmöglichkeiten der analytischen Nützung von "klassischen" Farbstoffen (d.h. von Farbstoffen, welche keine sehr feste Chelate bilden) bei der Lösung des verfolgten Problems hin. Auf Grund der Erkenntnis dieser Möglichkeiten sowie der Eigenschaften einzelner störender Komponenten, die in dieser Arbeit während ihrer nacheinander folgenden Beseitigung ersichtlich wurden, wird in der Zukunft eine größere Aufmerksamkeit denjenigen Farbstoffen gewidmet, die sehr stabile Chelate bilden. Man kann nämlich erwarten,[17] daß sie eine noch einfachere Bestimmung von Fluor als das vorgeschlagene Verfahren ermöglichen. Nach einer erfolgreichen Lösung der angedeuteten Bestimmungsweise,[17] bei welcher manche Erfahrungen aus der vorliegenden Arbeit völlig ausgenützt werden (z.B. die Art der Feststellung der Eichkurve), wird das vorgeschlagene Verfahren als Kontrollmethode dienen. Bei den Analysen der glücklicherweise nur sehr selten vorkommenden Wässern mit ungewöhnlich hohem Sulfat-Gehalt (z.B. das Zaječice-Bitterwasser, Böhmen, enthält 23,8 g SO_4^{2-}/kg) wird es dann auch weiterhin notwendig sein, zur Fällung der Sulfate diejenigen Kenntnisse anzuwenden, die zum Kernpunkt der vorliegenden Arbeit wurden.

Herrn Jiří Obermajer und Frau Jarka Hašková sei Dank ausgedrückt für ihre Hilfe bei der Durchführung der Experimente.

Summary—A highly sensitive spectrophotometric and photometric method for the determination of fluoride is described, based on the decolorisation of the zirconium-Eriochromcyanine lake in 0·2*N* hydrochloric acid. Interference from large amounts of sulphate is prevented by precipitating sulphate from slightly acidic solution. In these conditions no co-precipitation of fluoride occurs even in solution high in bicarbonate and silicic acid. Fluoaluminate is decomposed by alkali. The formation of an interfering iron^{III} dye complex is prevented by allowing the precipitation of ferric hydroxide after carbon dioxide is expelled.

Résumé—Les auteurs décrivent une méthode spectrophotométrique et photométrique très sensible pour le dosage du fluorure; cette méthode est basée sur la décoloration de la laque zirconium-ériochromecyanine dans l'acide chlorhydrique 0,2 N. L'interférence de grandes quantités de sulfate est

empêchée en précipitant le sulfate en solution faiblement acide. Dans ces conditions, le fluorure ne précipite pas, même en solution concentrée en bicarbonate et acide silicique. Le fluoaluminate est décomposé par les alcalis. La formation d'un complex coloré gênant du fer (III) est empêchée en réalisant la précipitation de l'hydroxyde ferrique après avoir chassé l'anhydride carbonique.

LITERATUR

[1] R. Valach, *Talanta*, 1961, **8**, 629.
[2] S. Megregian, *Analyt. Chem.*, 1954, **26**, 1161.
[3] L. L. Thatcher, *ibid.*, 1957, **29**, 1709.
[4] J. Mayer u. E. Hlucháň, *Chem. zvesti*, 1958, **12**, 143.
[5] Gautier u. Clausman, *Compt. rend.*, 1912, **154**, 1469, 1670, 1753; ref. in Gmelins *Handbuch der anorg. Chem.*, No 5-*Fluor*, Leipzig, Berlin, 1926.
[6] J. Bjerrum, G. Schwarzenbach u. L. G. Sillén, *Stability Constants*, Part 2. Chemical Society, London, 1958.
[7] L. Singer u. W. D. Armstrong, *Analyt. Chem.*, 1959, **31**, 105.
[8] B. Z. Senkowski, F. G. Wollish, u. E. G. E. Shafer, *ibid.*, 1959, **31**, 1957.
[9] A. Jílek u. J. Kota, *Vážková analysa a elektroanalysa*, *SNTL*, Vol. 3. Praha, 1956, p. 263.
[10] F. Richter, *Z. analyt. Chem.*, 1942, **124**, 192.
[11] M. L. Nichols u. A. C. Condo, *Analyt. Chem.*, 1954, **26**, 703.
[12] Z. Novák, *Zpráva o dos. činnosti na resort úkolech Oýzk. úst. vodoh-ospodářského*, Praha, 1959, *Fluorisace pitných vod ČSR.*
[13] K. Hayashi, T. Danzuku u. K. Ueno, *Talanta*, 1960, **4**, 126.
[14] Amer. Public Health Assoc., Amer. Water Works Assoc., Amer. Federation of Sewage and Ind. Wastes, New York, *Standard Methods for Examination of Water, Sewage and Industrial Wastes*, 10th ed., 1955, pp. 98–107.
[15] *Ministerstvo potrav. prům., Praha*, JAM č. 2, pp. 61–62, 1953.
[16] S. Megregian u. F. J. Maier, *J. Amer. Water Works Assoc.*, 1952, **44**, 239.
[17] R. Valach, *Talanta*, 1961, **8**, 443.

Talanta, 1962, Vol. 9, pp. 349 to 353. Pergamon Press Ltd. Printed in Northern Ireland

THE DETERMINATION OF TRACES OF RUTHENIUM IN SAMPLES OF PLATINUM BY NEUTRON-ACTIVATION ANALYSIS

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Summary—A neutron-activation method has been developed for determining small amounts of ruthenium impurity in samples of platinum. The Harwell nuclear reactor BEPO has been used as the source of neutrons. The procedure depends on the chemical separation of radioactive ruthenium, with added ruthenium carrier, from irradiated samples and standards. Results are quoted for the ruthenium contents of a number of samples of platinum.

THE work described in this paper forms part of a research programme on the development of new methods for the analysis of trace impurities in precious metals.[1–5] Relatively little has been reported previously on the determination of ruthenium by neutron-activation analysis. Leddicotte *et al.*[6] of the Oak Ridge National Laboratory, U.S.A., have indicated that radioactivation has been applied to the determination of small amounts of ruthenium in lithium iodide and report concentrations of 1–3 ppm. Miller,[7] working at the same establishment, has written a report on neutron-activation analysis applied to elements of Periodic Group VIII; his dissertation provides some general information on the determination of ruthenium.

With a thermal neutron flux of 10^{12} neutrons/cm^2/sec, as is available in the Harwell Pile BEPO, it has been estimated[8] that *ca.* 10^{-9} g of ruthenium may be determined under ideal conditions. This is below the limits of sensitivity of most other analytical methods for determining the element.[9,10]

Neutron-activation of ruthenium

Naturally occurring ruthenium consists of seven isotopes: ^{96}Ru (5·57%), ^{98}Ru (1·91%), ^{99}Ru (12·7%), ^{100}Ru (12·7%), ^{101}Ru (17·0%), ^{102}Ru (31·5%) and ^{104}Ru (18·5%). Some of these isotopes give rise to radionuclides when subjected to irradiation with thermal neutrons. The production and decay of the radionuclides is represented by the following sequences:

$$^{96}\mathrm{Ru(n,\gamma)}^{97}\mathrm{Ru} \xrightarrow[t_{1/2}=2{\cdot}88\ \mathrm{day}]{\mathrm{EC}} {}^{97m}\mathrm{Tc} \xrightarrow[t_{1/2}=91\ \mathrm{day}]{\mathrm{IT}} {}^{97}\mathrm{Tc} \xrightarrow[t_{1/2}=2{\cdot}6\times10^{6}\ \mathrm{yr}]{\mathrm{EC}} {}^{97}\mathrm{Mo}$$

$$^{102}\mathrm{Ru(n,\gamma)}^{103}\mathrm{Ru} \xrightarrow[t_{1/2}=39{\cdot}8\ \mathrm{day}]{\beta^-} {}^{103m}\mathrm{Rh} \xrightarrow[t_{1/2}=57\ \mathrm{min}]{\mathrm{IT}} {}^{103}\mathrm{Rh}$$

$$^{104}\mathrm{Ru(n,\gamma)}\ ^{105}\mathrm{Ru} \xrightarrow[t_{1/2}=4{\cdot}5\ \mathrm{hr}]{\beta^-} {}^{105m}\mathrm{Rh} \xrightarrow[t_{1/2}=45\ \mathrm{sec}]{\mathrm{IT}} {}^{105}\mathrm{Rh} \xrightarrow[t_{1/2}=36{\cdot}5\ \mathrm{hr}]{\beta^-} {}^{105}\mathrm{Pd}$$

Relevant thermal neutron-activation cross-sections, σ (barn), are:[11]

$$^{96}Ru \qquad \sigma = 0{\cdot}21$$

$$^{102}Ru \qquad \sigma = 1{\cdot}44$$

$$^{104}Ru \qquad \sigma = 0{\cdot}7.$$

Information on the decay of the radionuclides, including references to the original literature, is given by Strominger, Hollander and Seaborg.[12]

The absorption cross-section of platinum for thermal neutrons is high (8·8 barn) compared with that for ruthenium, (2·56 barn). To avoid shelf-shielding differences between samples and standards in the present work, standards were, therefore, prepared by the addition of small known quantities of ruthenium to analytical samples.

EXPERIMENTAL

Irradiation

Specimens of platinum sponge for analysis had been broken down to a powder and 0·1-g samples were accurately weighed and sealed in silica irradiation tubes of 4-mm internal diameter. Standards were prepared by the addition of weighed portions (*ca.* 0·05 g) of a standard solution of ruthenium (10 mg of ruthenium per litre of 3*M* hydrochloric acid) to 0·1 g samples of platinum in silica irradiation tubes. The liquid was allowed to soak into the metal powder, then was carefully evaporated to dryness, after which the tubes were sealed.

Samples, together with standards containing added ruthenium, were packed in silica wool in standard aluminium screw-top cans and were sent to the Atomic Energy Research Establishment, Harwell, for neutron activation. Irradiations were for a period of 1 week in the nuclear reactor BEPO with a thermal neutron flux of $1{\cdot}2 \times 10^{12}$ neutrons/cm^2/sec.

Radiochemical procedure

In the radiochemical procedure for the separation of ruthenium from samples and standards following neutron irradiation, inactive ruthenium was employed as a carrier. The material used for the carrier was checked for freedom from radioactive contamination, because ruthenium produced in recent years has been shown to contain ^{106}Ru from "fall-out" from nuclear explosions.[13]

Many radiochemical procedures for ruthenium are available and a number of them are appended in a recent monograph on the radiochemistry of the element.[14] However, a new procedure utilising solvent extraction and based in part on the work of Surasiti[15,16] was developed for the present study.

Special reagents

Ruthenium carrier:[17] Dissolve 0·75 g of ruthenium chloride* in 50 ml of water, then add 5 g of sodium hydroxide and 2 g of potassium persulphate. Heat to boiling. When the precipitate has dissolved, add 0·5 ml of methyl alcohol and stir thoroughly. Digest the mixture near the boiling point until the precipitate coagulates, then centrifuge the solution and discard the supernate. Wash the precipitate once with boiling water and dissolve it in 50 ml of hot 2·5*M* sodium hydroxide solution containing 2 g of potassium persulphate. Cool and dilute to *ca.* 100 ml. Add 2 ml of the prepared carrier solution to 5 ml of potassium periodate-potassium hydroxide reagent (see below) in a 50 ml calibrated flask and dilute to volume. Measure the optical absorbancy of this solution in a 1-cm cell at 4700 Å. Dilute the ruthenium carrier solution by proportion so that the absorbancy of a 2-ml aliquot in the alkaline periodate reagent lies between 0·6 and 0·8. Prepare a calibration chart using 0·5, 1·0, 1·5, and 2 ml of the final ruthenium carrier solution to determine the optical absorbancy.

Potassium periodate-potassium hydroxide reagent: Dissolve 20 g of potassium hydroxide and 10 g of potassium periodate in 200 ml of water.

Osmium carrier: Dissolve a weighed quantity of pure recrystallised ammonium hexachloro-osmate in dilute hydrochloric acid to give a solution containing 1 mg of osmium/ml.

Gold carrier: Prepare a solution containing 1 mg of gold/ml in dilute hydrochloric acid.

* Beta-count this material for a considerable period to ensure its freedom from $^{106}Ru - ^{106}Rh$.

Carbon tetrachloride: Shake analytical reagent material with 0·1*N* potassium permanganate in 2*M* sulphuric acid for several hr. Separate the phases and shake the carbon tetrachloride with several portions of concentrated sulphuric acid and once with water. Saturate the carbon tetrachloride with chlorine and reflux for a few hr. Remove chlorine by shaking with several portions of 2*M* potassium hydroxide. Wash the carbon tetrachloride with water until neutral to litmus paper, dry with Anhydrone, and distil. Store in the dark.

Silver^{II} oxide: Prepare this by boiling a solution of silver nitrate with a strong potassium hydroxide solution of potassium persulphate until evolution of oxygen ceases, wash with hot water, and dry over a desiccant.

Separation procedure

Dissolution of the irradiated platinum. Remove the irradiation tubes from the can, open them, and transfer the samples and standards quantitatively to 150-ml beakers each containing 2 ml of standard ruthenium carrier and 3 ml of 12*M* hydrochloric acid. In every case wash out the tube thoroughly with hot 6*M* hydrochloric acid and add the washings to the respective beaker. Add 1 ml of 16*M* nitric acid to the contents of each beaker and slowly dissolve the platinum by warming on a hot-plate. When the platinum has dissolved, add two successive 1-ml portions of 12*M* hydrochloric acid and heat to remove nitric acid.

Removal of osmium. Add 1 ml of osmium carrier and 15 ml of 6*M* sulphuric acid and evaporate to fumes. Continue fuming moderately for *ca.* 1 hr. Cool and transfer the solution to a 50-ml centrifuge tube containing 15 ml of water. Cool and add 0·1*N* potassium permanganate solution until a pink colour remains. Destroy excess permanganate by adding 50 mg of iron^{II} ammonium sulphate hexahydrate dissolved in a little water. Without delay add 15 ml of 16*M* nitric acid and extract osmium tetroxide into three successive 10-ml portions of carbon tetrachloride. Separate and discard the organic layers, retaining the aqueous phase.

Oxidation and extraction of ruthenium. Add, with stirring, sufficient silver^{II} oxide to the aqueous solution to give a brown colour. Allow to stand for 10 min to ensure complete oxidation of ruthenium to the tetroxide. Extract with three 10-ml portions of carbon tetrachloride. Combine and retain the organic layers in a clean 50-ml centrifuge tube. Wash the combined extract twice with 10-ml portions of 2*M* sulphuric acid containing a little silver^{II} oxide. Separate the organic phase and discard the wash solutions. Return ruthenium from the organic phase to aqueous solution by agitating the carbon tetrachloride extract with 10 ml of 3*M* sodium hydroxide solution to which has been added 2 drops of 5% sodium dithionite solution. Separate the aqueous layer into a clean 50-ml centrifuge tube.

Removal of gold. Acidify the solution with hydrochloric acid, add 1 ml of gold carrier, and extract the gold with three 10-ml portions of ether. Retain the aqueous phase and make it alkaline with 6*M* sodium hydroxide solution.

Precipitation of the ruthenium for counting. Add 2 ml of industrial methylated spirit and mix thoroughly, Digest on a stream bath until the precipitate of ruthenium dioxide has coagulated. Centrifuge and discard the supernate. Wash the precipitate with portions of water and alcohol. Slurry it with a little alcohol on to an aluminium counting tray using a dropping pipette fitted with a rubber bulb. Evaporate off the alcohol under a radiant-heater lamp. The precipitate is then ready for counting.

Determination of the chemical yield. After counting measurements on the final precipitates have been performed, determine the chemical yield for each sample and standard as follows. (This part of the procedure must be carried out strictly quantitatively and without loss). Remove the bulk of the ruthenium dioxide from a counting tray by tapping the solid into a 50-ml beaker. Dissolve the remainder using 5 ml of potassium hydroxide-potassium periodate reagent, allowing the reagent to flow slowly from a dropping pipette across the tray and into the beaker. Rinse the tray with a few drops of distilled water, and collect the washings in the beaker. Warm to complete solution if necessary and transfer quantitatively to a 50-ml calibrated flask and make to the mark with water. Measure the optical absorbancy at 4700 Å in a 1-cm cell. Obtain the chemical yield by reference to the absorbancies determined for known aliquots of the ruthenium carrier solution.

Measurement of radioactivity of the final precipitates

The final precipitates of ruthenium dioxide from the irradiated samples of platinum and from the standards were counted under similar conditions with a Geiger-Müller counter of the EHM 2/S type. All measured counting rates were corrected for paralysis, background, and chemical yield and for any decay of significance between counting samples and standards.

The radiochemical purity of the sources was checked by decay and gamma-spectrometric measurements. The measured γ-ray energies and half-lives corresponded with those obtained from a sample of neutron-irradiated pure ruthenium.

RESULTS

In Table I are shown results of analyses of samples of platinum. No ruthenium could be detected in these specimens by emission spectrographic analysis.

TABLE I.—RUTHENIUM CONTENTS OF SAMPLES OF PLATINUM DETERMINED BY NEUTRON-ACTIVATION ANALYSIS

Sample	Ruthenium content, *ppm*
Pt 1	1·03, 1·07
Pt 2	1·96, 1·92
Pt 3	0·83, 0·86
Pt 4	0·97, 0·93
Pt 5	1·61, 1·50, 1·70, 1·51
Pt 6	1·09, 1·12
Pt 7	1·75, 1·78

DISCUSSION

In the neutron-activation analysis of ruthenium in samples of platinum consideration must be given to the possibility of formation of radionuclides used in the analysis from activation of elements other than ruthenium in the samples.

Thus possible interference might arise from the following nuclear reactions of rhodium and palladium:

$$^{103}\mathrm{Rh(n, p)}^{130}\mathrm{Ru}$$

$$^{106}\mathrm{Pd(n, \alpha)}^{103}\mathrm{Ru}$$

$$^{108}\mathrm{Pd(n, \alpha)}^{105}\mathrm{Ru}.$$

These reactions could occur with the fast flux of neutrons associated with the thermal neutron flux within the reactor BEPO. Under the irradiation conditions employed in the present work this fast neutron flux was 2×10^{11} neutrons/cm^2/sec. Interference from the nuclear reactions was shown to be unimportant, however, by analysing by activation samples of platinum Pt 6 to which had been added 0·3 μg of rhodium and 0·3 μg of palladium. The results obtained were 1·02, 1·05, 0·99 and 1·09 ppm of ruthenium which agree well with the analyses of platinum Pt 6 listed in Table I.

Possible interference from the nuclear reactions:

$$\mathrm{U(n, f)}^{103}\mathrm{Ru}$$

$$\mathrm{U(n, f)}^{105}\mathrm{Ru}$$

$$\mathrm{U(n, f)}^{106}\mathrm{Ru}$$

has been discounted because the samples of platinum analysed are unlikely to contain more than negligible amounts of uranium.

Acknowledgement—We are grateful to The International Nickel Company (Mond) Ltd., for the supply of precious metals, for financial support, and for a Research Fellowship to one of us (R. A. K.).

Zusammenfassung—Eine auf Neutronenaktivierung beruhende Methode zur Bestimmung von Rutheniumspuren in Platin wurde entwickelt. Der Harwell-Reaktor BEPO diente als Neutronenquelle. Radiochemische Trennungen nach Zugabe von Ruthenium als Träger, wurden auf Probe und Standard angewandt. Resultate für einige Proben werden mitgeteilt.

Résumé—Les auteurs ont mis au point une méthode de dosage, par activation neutronique, de faibles quantités d'impureté de ruthénium dans des échantillons de platine. Le réacteur nucléaire BEPO de Harwell a été utilisé comme source de neutrons. La méthode dépend de la séparation chimique du ruthénium radioactif, à l'aide d'un entraîneur, des échantillons irradiés et des étalons. Les résultats cités donnent les teneurs en ruthénium d'un certain nombre d'échantillons de platine.

REFERENCES

[1] D. F. C. Morris and R. A. Killick, *Talanta*, 1959, **3**, 34.
[2] *Idem*, *Ibid.*, 1961, **8**, 129.
[3] D. F. C. Morris, D. N. Slater, and R. A. Killick, *Ibid.*, 1961, **8**, 373.
[4] R. A. Killick and D. F. C. Morris, *Ibid.*, 1961, **8**, 601.
[5] *Idem*, *ibid.*, 1961, **8**, 793.
[6] G. W. Leddicotte, W. T. Mullins, L. C. Bate, J. F. Emery, R. E. Druschel and W. A. Brooksbank, *Progr. Nuclear Energy*, Series *IX*, 1959, **1**, 123.
[7] C. E. Miller, U.S. Atomic Energy Comm. Report, ORNL-2715, 1959.
[8] E. N. Jenkins and A. A. Smales, *Quart. Rev.*, 1956, **10**, 83.
[9] W. W. Meinke, *Science*, 1955, **121**, 177.
[10] J. W. Winchester, *Progr. Inorg. Chem.*, 1960, **2**, 1
[11] D. J. Hughes and R. B. Schwartz, U.S. Atomic Energy Comm. Compilation. BNL 325, 2nd Ed. 1958.
[12] D. Strominger, J. M. Hollander and G.T Seaborg, *Rev. Mod. Phys.*, 1958, **30**, 585.
[13] J. R. De Voe, U.S. National Academy of Sciences-National Research Council, Publication 895, 1961.
[14] E. I. Wyatt and R. R. Rickard, Nuclear Sciences Series Monograph, NAS-NS 3029, 1961.
[15] C. Surasiti, Ph.D. Thesis, University of Minnesota, 1957.
[16] E. B. Sandell, *Colorimetric Determination of Traces of Metals*. Interscience Publishers, New York, London, 3rd Ed., 1959.
[17] B. A. Loveridge and A. M. Thomas, Atomic Energy Research Establishment, Harwell, report, AERE C/R 2828, 1959.

Talanta, 1962, Vol. 9, pp. 355 to 364. Pergamon Press Ltd. Printed in Northern Ireland

AN INVESTIGATION OF SODIUM 5-(3-NITROPHENYLAZO)SALICYLATE AS A SPECTROPHOTOMETRIC REAGENT FOR MAGNESIUM

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Summary—Sodium 5-(3-nitrophenylazo)salicylate reacts almost specifically with magnesium ions (at pH 10·5) to give a yellow coloured chelate. The solution has an absorbance maximum at 450 mμ. The sensitivity of the reaction is 0·01 μg of magnesium per cm² for log $I_0/I = 0·001$. Optimum conditions for the reaction have been established. Development of the spectrophotometric method for the determination of magnesium included a study of the effect of pH, the ratio of reagent to magnesium, photometric stability of the complex, its conformity to Beer's law, and the rate of colour formation. The method has been applied successfully to the determination of magnesium in silica brick and silicon-aluminium alloy.

A RECENT critical review[1] of the analytical chemistry of magnesium cites only three chelating agents suitable for its spectrophotometric determination. These are Eriochrome Black T,[2–5] 2-[2-hydroxy-3-(2,4-xylylcarbamoyl)]-1-naphthalazophenol[6] and its sulphate,[7] and 8-quininol.[8] Consequently, when the spot test procedure of Yoe[9] showed that sodium 5-(3-nitrophenylazo)salicylate reacted almost specifically with ammoniacal magnesium to give a yellow colour, it was decided to examine the nature of the complex and to assess its worth as a reagent for the spectrophotometric determination of magnesium.

EXPERIMENTAL

Apparatus

Spectrophotometers: Beckman Spectrophotometers, Models DU and DK-2, with matched 1-cm Corex or quartz cells.

pH Meter: Beckman Model G, with general purpose glass electrode.

Reagents

Sodium 5-(3-Nitrophenylazo)salicylate (NPAS): Obtained from Eastman Kodak; the solid is brick red. In solution it acts as a pH indicator, being yellow below pH 10 and wine red above pH 12. (The colour change is not sufficiently sharp to make it a useful indicator). Below pH 9 its solubility is about 0·02 g/l., and at pH 10·5 it is about 0·065 g/l. Solutions continuously exposed to light are slightly unstable but those kept in polyethylene bottles in a cupboard are stable for at least 3 weeks. The solution used for routine determinations was about saturated and was prepared by weighing out 0·065 g of NPAS, adding 500 ml of pH 10·5 buffer (see below), making up to 1 litre and filtering into a polyethylene bottle. More dilute standard solutions were prepared for mole ratio determinations.

Standard Magnesium Solution: Magnesium oxide ("Baker analysed" A.C.S.) was ignited and cooled in a desiccator. 1·6582 g was dissolved in the smallest possible amount of hydrochloric acid and made up to 1 litre with triply-distilled water. This solution contained 1 g of magnesium as was confirmed by titrating with EDTA.

Buffer Solutions: (1) pH 10: Fisher standard buffer was used to set the pH meter for readings in the pH 10 region. (2) pH 10·5: The sodium borate-carbonate mixture of Kolthoff and Vleeschhouwer[10] was used. A mixture of 89 ml of carbonate solution (5·3 g of anhydrous sodium carbonate/l.; 0·05*M*) and 11 ml of borax solution (19·1 g of borax/l.; 0·05*M*) has a pH of 10·5.

Solutions of Diverse Ions: Reagent grade salts were used to prepare solutions of various ions. The stock solutions generally contained 1 g of the ion per litre of solution.

Acetylacetone: Reagent grade acetylacetone was used as a 25% v/v solution in AnalaR carbon tetrachloride.

Water: Triply-distilled.

Nitric Acid: C.P., doubly distilled.

Hydrochloric Acid: AnalaR, distilled four times.

Ammonia: C.P. Other reagents were made up from the best quality material available and used without further purification.

DETERMINATION OF OPTIMUM CONDITIONS

Preliminary tests showed that at about pH 10·5 when the reagent solution is an orange-red colour, the magnesium complex is yellow. The absorption curves (Fig. 1) indicated that it should be possible to determine magnesium despite the high reagent absorption. Since the colour of the reagent is markedly pH dependent in the region of 10 to 12, changing its absorption peak from 372 mμ to 479 mμ (Fig. 2), it was expected that its magnesium complex would also be pH dependent.

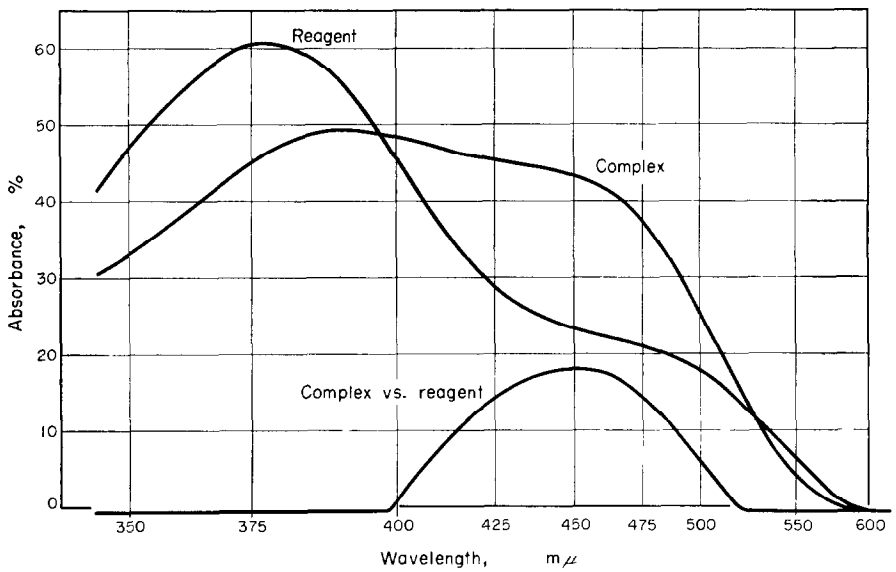


FIG. 1.—Absorption curves at pH 10·5 for reagent against water, complex against water, and complex against reagent.

Effect of pH

Fig. 2 shows the dependence of the complex on pH ("apparent" pH) in a buffered solution. In an unbuffered solution a curve of similar shape was obtained with the peak at pH 10·2. This might be because an increase in ionic strength hinders the formation of the magnesium complex as it does the precipitation of magnesium hydroxide. The sharp fall off in absorption is almost certainly caused by hydroxide precipitation. However, other conditions affect the choice of optimum pH. It is preferable that the reagent absorption at 450 mμ be constant for small changes in pH. This condition is best realised at pH 10·5. The buffer system employed required that the pH be adjusted by hydroxide addition to a value close to that of the final pH. The possibility of hydroxide precipitation before complex formation increases, therefore, with a higher final pH value. Furthermore, since a carbonate-borate buffer is preferred, a higher

pH means a higher carbonate concentration, with greater chance of calcium interference. Hence pH 10·5 was adopted as a working pH, with some loss in sensitivity and flexibility. All pH values are uncorrected for ionic concentration.

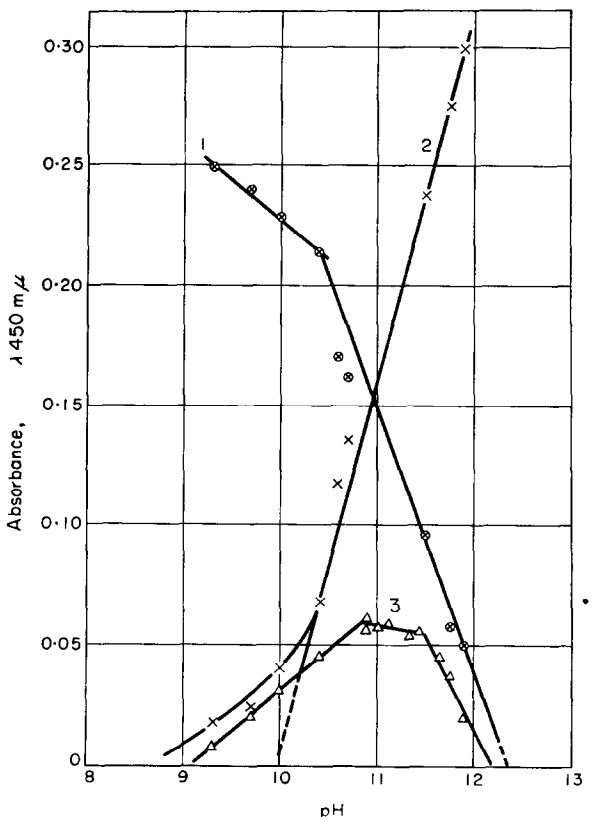


FIG. 2.—(1) Absorption of reagent at 372 mμ against pH,
(2) absorption of reagent at 479 mμ against pH,
(3) complex absorption at 450 mμ against pH.

Choice of buffer

Following the preceding argument, one might ask why either a Sörensen glycine–sodium chloride–sodium hydroxide buffer or an ammonia–ammonium chloride buffer was not employed. In the presence of a Sörensen buffer, calcium interferes by forming a coloured complex. The use of the ammonia buffer enhanced phosphate interference and slightly lowered the sensitivity of the method. As will be discussed later, the carbonate buffer is tolerant towards these interferences. If the sample is calcium-free, the Sörensen buffer would be suitable.

Order of addition of reactants

In the absence of alkaline earth ions the order of addition of the three reactants, magnesium, NPAS and buffer, does not matter. If the alkaline earths are present, the NPAS and buffer must be mixed before being added to the sample solution. This is necessary because the addition of carbonate buffer to the solution of the magnesium and alkaline earths, either before or after the addition of NPAS, results in turbidity or precipitation.

Stability of colour

The colour is formed rapidly and is fairly stable. The absorption falls off by about 1% after 1 hr and 13% after 4 days.

Beer's law and sensitivity

The range over which Beer's law is obeyed varies with the conditions and the amount of reagent used. With the recommended amount the range is from 0·05 to 2·5 ppm of magnesium in pure solutions. If the solution is treated extensively beforehand, *e.g.*, by repeated precipitations or extractions, the range may fall to 0·05–1·0 ppm; but the sensitivity remains the same and is 0·01 μg of magnesium per cm^2 for log $I_0/I = 0{\cdot}001$. As can be seen from the mole ratio curve, (Fig. 3),

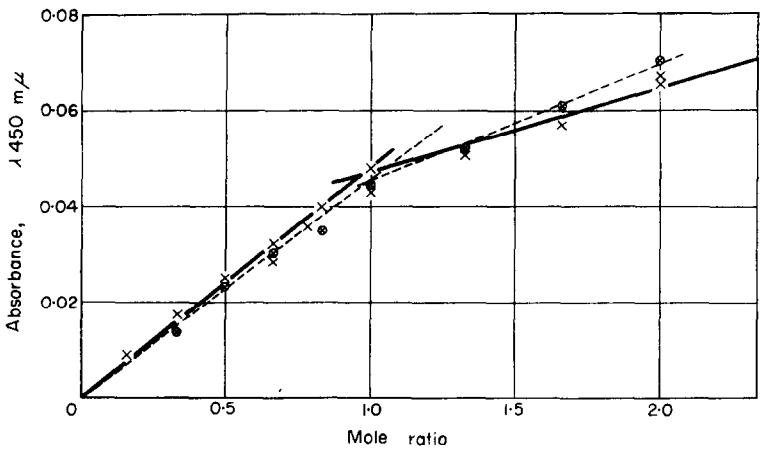


FIG. 3.—Mole ratio and "reverse" mole ratio:
⊗ = 3 × 10^{-7} moles of magnesium with varying amounts of NPAS.
× = 3 × 10^{-7} moles of NPAS with varying amounts of magnesium.

the absorbance continues to increase with further addition of magnesium. The curve is linear up to 8 ppm and the sensitivity in this range is 0·38 μg of magnesium/cm^2. If two thirds of the reagent concentration is used, the sensitivity is approximately halved whilst the range is nearly doubled. The extent to which the sensitivity may be increased by increasing the reagent concentration is limited by its solubility and absorption at 450 mμ.

Structure of the magnesium complex

The mole ratio method of Yoe and Jones[11] (Fig. 3) and Job's[12] method of continuous variations as modified by Vosburgh and Cooper[13] (Fig. 4) indicates a 1:1 complex. The reagent is too insoluble and too intensely coloured to permit the use of the Harvey and Manning[14] slope-ratio method, which requires a large constant excess. But the "reverse" mole ratio method adopted (Fig. 3) indicates (by the absence of breaks) no higher complexes. Mole ratio studies also indicate that the complex is weak. EDTA readily destroys the complex but the colour change involved is not sufficiently sharp to warrant using NPAS as an indicator in the EDTA titration of magnesium. The second pK value[15] for salicylic acid is about 13. Hence

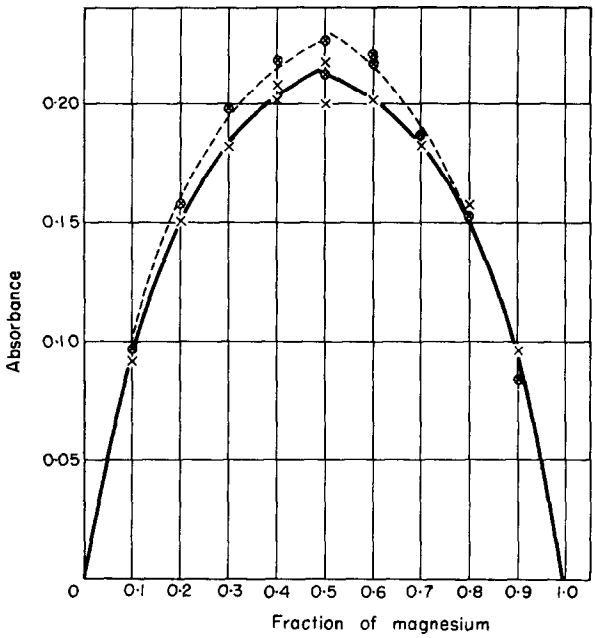


FIG. 4.—Continuous variations (15×10^{-5} *M*; pH 10·4):
× = 440 mμ: ⊗ = 475 mμ.

it seems reasonable to postulate the structure of the chelate as shown in Fig. 5. Waters of co-ordination almost certainly take up the remaining co-ordination positions.

Effect of diverse ions

The reagent was tested on the spot plate with seventy-eight different ions, buffered at pH 10·5. Only calcium formed a colour with the reagent. Quantitative estimates of interferences were made by adding the interfering ion to a magnesium solution, which was then analysed by the proposed procedure. This showed that although only calcium gives a colour, every ion which was present in sufficient concentration

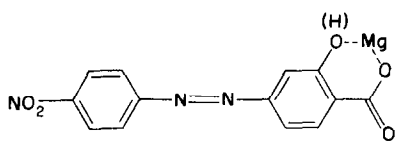


FIG. 5.—Proposed structure of the magnesium complex of 5-(3-nitrophenylazo)salicylic acid (waters of co-ordination omitted).

to precipitate at pH 10·5 caused an error, either by coprecipitation or by turbidity. Hence most cations must be removed from solution before determining the magnesium.

When magnesium is present at a concentration of 1 ppm, phosphate up to 100 ppm does not cause more than 10% interference. If present at a concentration of 0·5 ppm, less than 10% interference is caused by 0·1*M* chloride, 0·01*M* sulphate, 0·01*M* acetate, 0·01*M* nitrite and 0·001*M* nitrate, respectively. The molarities refer to the final solution.

Interference of alkaline earths

The effects of the alkaline earths upon the reaction were so unusual that they were investigated more fully. In the presence of an ammonia or Sörensen buffer (*vide ultra*) the calcium complex absorbs at the same wavelength at which the magnesium complex absorbs but the sensitivity is only a tenth of that for magnesium. The effect of calcium on the absorption of the magnesium complex in the presence of a carbonate buffer is shown in Fig. 6. Barium and strontium behave similarly. The slight initial increase in absorption may be caused by either complex formation or turbidity from a suspension of finely divided calcium carbonate; the absorption

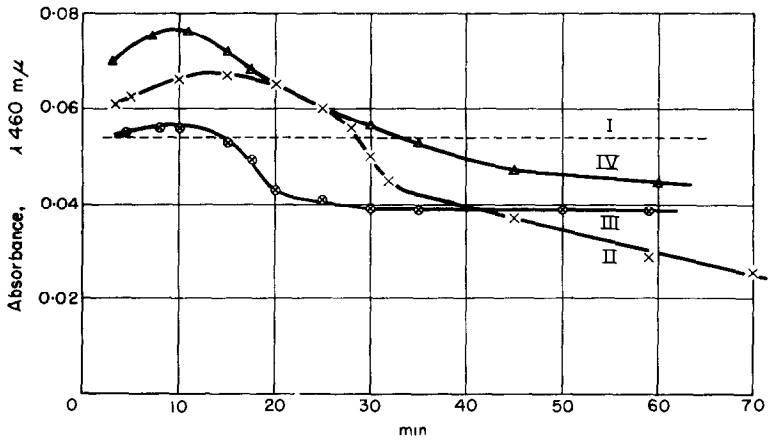


FIG. 6.—Effect of alkaline earths on absorption of the magnesium complex: (I) 1 ppm of Mg; (II) 1 ppm of Mg, 40 ppm of Ca; (III) 1 ppm of Mg, 30 ppm of Sr; (IV) 1 ppm of Mg, 40 ppm of Ca, 40 ppm of Sr.

lowering may be ascribed to the precipitation of the carbonate with coprecipitation of the magnesium. Because the system is not completely reproducible, the minimum amount of calcium needed to cause this type of interference could not be established precisely. Sometimes 20 ppm could be tolerated and other times it could not, but 40 ppm in every case caused a lowering of the absorption. It was found, however, that if calcium, strontium and barium are added at a level of 40 ppm each, the absorption remained constant and correct (Fig. 7). Further experiments showed that:

(1) All three alkaline earths had to be present for the stabilising effect to be noticed (Fig. 7). If only two of the alkaline earths were present the behaviour was about the same as if only one was present.

(2) The buffer solution must be mixed with the reagent before addition. If it is added separately the solution becomes turbid.

(3) When barium and strontium are added the maximum amount of calcium that can be tolerated with certainty is 40 ppm. This can be held up by almost any combination of barium or strontium from 5 ppm of each to 5 ppm of barium with 40 ppm of strontium. With 1 ppm of magnesium an error of less than 10% was noted in most instances, if the reading was taken within 20 min from the time of mixing.

(4) Barium and strontium prevented calcium interference when the concentrations of magnesium or buffer are varied.

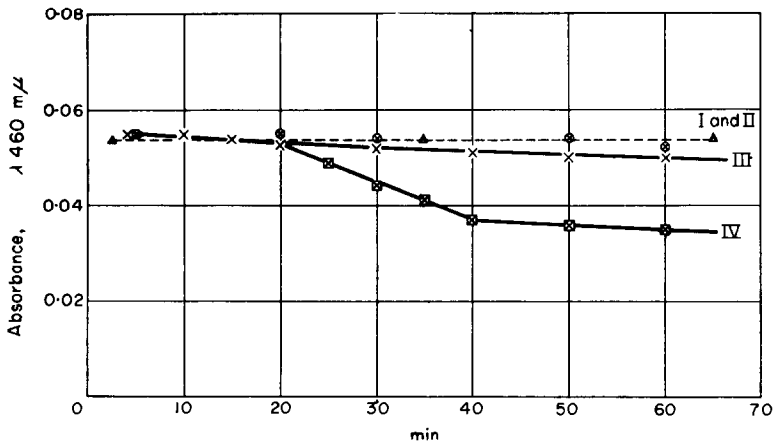


FIG. 7.—Effect of mixtures of alkaline earths on absorption of the magnesium complex: (I) 1 ppm of Mg; (II) 1 ppm of Mg, 40 ppm of Ca, 40 ppm of Sr, 40 ppm of Ba; (III) 1 ppm of Mg, 40 ppm of Ca, 20 ppm of Sr, 20 ppm of Ba; (IV) 1 ppm of Mg, 40 ppm of Ca, 10 ppm of Sr, 5 ppm of Ba.

(5) Each curve is not exactly reproducible. The shape of the curve is similar and the rate of drop in absorption is the same but the point at which the decline begins may vary.

From these results it was concluded that the effect was probably caused by supersaturation, although it could not be fully explained. In practice it was thought that calcium interference could be overcome by adding 20 ppm each of strontium and barium and reading after 15 min. It was found, however, in the analysis of solutions containing various ions, that after the necessary separations had been made, calcium up to 40 ppm does not interfere.

ANALYSIS OF COMPLEX MIXTURES

All spectrophotometric methods for determining magnesium require the prior separation of other ions. Three ways were investigated:

(1) *Extraction with 8-quinolinol.* At pH 5 to 7, 8-quinolinol extracts many metals into chloroform or carbon tetrachloride.[16] It has been used as a means of removing interferences prior to a colorimetric determination of magnesium.[7] We found that results were a little low, probably because of incomplete removal of 8-quinolinol, and so the other two procedures are preferred.

(2) *Extraction with acetylacetone.* Between pH 3 and 7 acetylacetone extracts several ions into chloroform or carbon tetrachloride.[16] It has been used to remove interferences before making a magnesium determination.[17] The ions that are most effectively removed are those of aluminium, iron^{III}, copper, manganese, titanium, vanadium and uranium. If these ions and calcium are the only interferences procedure (2) was preferred because of its speed and ease.

(3) *Precipitation with ammonium hydroxide.* The classical double precipitation with ammonium hydroxide in the presence of ammonium chloride proved the most widely applicable method for the removal of interferences. Ammonia must be removed; this was done by evaporation to dryness with excess nitric acid.

ANALYSIS OF STANDARD SAMPLES

To test the efficiency of the method, two National Bureau of Standards samples of widely different composition were analysed.

NBS 102–*Silica Brick*

The principal interferences present and their percentages are SiO_2 (93·94), Al_2O_3 (1·96), CaO (2·29) and Fe_2O_3 (0·66). Other constituents present at the level of 0·01 to 0·3% are TiO_2, ZrO_2, MnO, Na_2O, K_2O and P_2O_5.

Procedure: Treat 1 g of the sample with hydrofluoric acid and a few drops of dilute sulphuric acid, and evaporate to dryness to remove the silica. Fuse the residue with sodium carbonate, take up the fusion mixture in dilute hydrochloric acid and add at least 10 ml of 70% perchloric acid. Evaporate the solution to dense fumes, then boil for 10 min. Add 30 to 40 ml of water, boil, filter and make up the filtrate to 100 ml. Take a 5-ml aliquot, adjust the pH to 3–4 with sodium bicarbonate and extract with 10 ml of acetylacetone solution (to remove the bulk of the iron), rejecting the organic layer. Adjust the pH to 7, extract twice more with acetylacetone, then with 10 ml of carbon tetrachloride. Make acid and extract twice more with carbon tetrachloride to remove the excess reagent. Transfer the aqueous layer to a small beaker, add a few drops of bromine water and evaporate to dryness. Take up the residue in water, adjust the pH to 9·0 to 9·5 with the aid of a pH meter and make up to 25 ml. Take a 2-ml aliquot, add 3 ml of NPAS solution, make up to 10 ml with water, mix, and read

TABLE I. ANALYSIS OF NBS 102
(MgO, 0·21%; range, 0·19–0·22%)

Sample No.	MgO, %
1	0·22[a]
2	0·215[b]
3	0·190[b]
4	0·207[c]
mean	0·208
stand. devn.	= 0·0264 or 12·6%

[a] Av. of 4 determinations;
[b] Av. of 5 determinations;
[c] Av. of 6 determinations.

the absorbance at 450 mμ after 15 min. Obtain the magnesium value from a calibration curve prepared by applying the same procedure to standard magnesium solutions. Results with NBS 102 are shown in Table I.

TABLE Ia. ANALYSIS OF VARIANCE FOR DATA FROM ANALYSIS OF NBS 102

Source of variation	Sum of squares	Deg. of freedom	Variance	Stand. devn.
Between samples	134	3	44·6	
Within samples	649	16	40·6	6·36
Total	783	19		

The table gives working units which are converted to % of MgO by adding 40 and multiplying by $4{\cdot}115 \times 10^{-3}$. Converting to % of MgO, stand. devn. = 0·0264 or 12·6%. Applying the F test,

$$\text{F ratio} = \frac{44{\cdot}6}{40{\cdot}6} = 1{\cdot}1$$

F values for 3 and 16 degrees of freedom for 5% and 1% are 3·24 and 5·29, respectively. Hence there is no reason to consider that the samples significantly differ.

NBS 87 *Aluminium–Silicon Alloy*

The main interferences in this sample are aluminium, silicon (6·21%), nickel (0·59%) and iron (0·46%). Others include copper, chromium, lead, manganese,

tin, titanium and zinc. The high concentration of aluminium and the presence of tin and zinc made the precipitation procedure more satisfactory than the extraction technique.

Procedure: Weigh about 0·3 g of sample and dissolve as much as possible in dilute hydrochloric acid. Filter, keep the filtrate, burn off the filter paper and fuse the residue with sodium carbonate. Treat the fused mixture with perchloric acid as before and filter. Combine the filtrate with the first filtrate and make up to 100 ml. Take a 5-ml aliquot and treat with ammonium hydroxide according to Hillebrand *et al.*[18] Remove the ammonia by adding 10 to 15 ml of concentrated nitric acid and evaporating to dryness. The procedure from this point is the same as for NBS 102. The results with NBS 87 are shown in Table II.

TABLE II. ANALYSIS OF NBS 87
(Mg, 0·39%; range, 0·37–0·40%)

Sample No.	Mg, %
1	0·373
2	0·382
3	0·362
mean	0·372
stand. devn. = 0·0364 or 9·7%	

Each value is the average of 4 determinations.

TABLE IIa. ANALYSIS OF VARIANCE FOR DATA FROM ANALYSIS OF NBS 87

Source of variation	Sum of squares	Deg. of freedom	Variance	Stand. devn.
Between samples	919	2	459·5	21·43
Within samples	11937	9	1324	36·4
Total	12856	11		

The table gives working units which are converted to % of Mg by adding 300 and multiplying by 1000. Converting to % of Mg, stand. devn. = 0·0364 or 9·7%. Applying the F test, F ratio = $\frac{1324}{459·5} = 2·88$.

F values for 9 and 2 degrees of freedom at 5% and 1% levels are 4·26 and 8·2, respectively. Therefore there is no reason to consider that the samples significantly differ.

Precision

To obtain the precision of the method in pure magnesium solutions, the same amount of magnesium was determined 11 times. The average absorption was 0·125 and the standard deviation 0·00094 or 0·7%. This precision is not obtained when a complex mixture is analysed. The data for the precision of two such analyses are given in Tables Ia and IIa. The values were obtained by following the statistical procedures recommended by Davies.[19] It can be seen that the precision for complex mixtures is about 10%. The difference between NBS 102 and NBS 87 probably reflects the longer experimental procedure, rather than a marked difference between the extraction and precipitation method of separation.

Zusammenfassung—5-(3-nitrophenylazo)salizylsäure (als Natriumsalz) reagiert be pH 10·5 nahezu spezifisch mit Magnesium unter Bildung eines gelb gefärbten Chelates. Die Lösung zeigt ein Absorptionsmaximum be 450 mμ. Die Empfindlichkeit der Reaktion ist 0·01 μg Magnesium per cm² für log $I_0/I = 0·001$. Die optimalen Bedingungen für die Reaktion wurden ermittelt. Die Ausarbeitung einer spektrophotometrischen Methode zur Bestimmung von Magnesium erfolgte auf Grund der Studien über Einfluss von pH der Lösung, Verhältnis Magnesium zu Reagens, Gültigkeit von Beer's Gesetz und Geschwindikeit der Farbentwicklung. Die Methode wurde mit Erfolg auf die Bestimmung von Magnesium in Ziegeln und Silizium-Aluminum Legierung angewendet.

Résumé—L'acide 5-(3-nitrophénylazo)salicylique (sel de sodium) réagit presque spécifiquement avec les ions magnésium (à pH 10,5) pour donner un chelate de couleur jaune. La solution a une absorption maximale à 450 mμ. La sensibilité de la réaction est 0,01 μg de magnésium par cm^2 pour log $I_0/I = 0{,}001$. Les conditions les meilleures de la réaction ont été établies.

La mise au point de la méthode spectrophotométrique de dosage du magnésium nécessite une étude de l'action du pH, du rapport réactif/magnésium, de la stabilité photométrique du complexe, de la vitesse de formation de la couleur; il faut, de plus, savoir si le complexe suit la loi de Beer.

La méthode a été appliquée avec succès au dosage du magnésium dans la brique de silice et dans l'alliage silicium-aluminium.

REFERENCES

[1] I. M. Kolthoff and P. J. Elving (Editors), *Treatise on Analytical Chemistry*. Interscience Publishers, New York, 1961. Part II, Vol. 3, pp. 43–93.
[2] A. E. Harvey, J. M. Kormamy and G. M. Wyatt, *Analyt. Chem.*, 1953, **25**, 498.
[3] W. Dirscherl and H. Breuer, *Mikrochem. Mikrochim. Acta*, 1953, **40**, 322.
[4] A. Young, T. R. Sweet and B. B. Baker, *Analyt. Chem.*, 1955, **27**, 356.
[5] A. Young and T. R. Sweet, *ibid.*, 1955, **27**, 418.
[6] C. K. Mann and J. H. Yoe, *Anal. Chim. Acta*, 1957, **16**, 155.
[7] C. K. Mann and J. H. Yoe, *Analyt. Chem.*, 1956, **28**, 202.
[8] F. Umland and W. Hoffmann, *Anal. Chim. Acta*, 1957, **17**, 234.
[9] J. H. Yoe, *J. Chem. Educ.*, 1937, **14**, 170.
[10] I. M. Kolthoff (translated by C. Rosenblum), *Acid-Base Indicators*. Macmillan, New York, 1937. p. 355.
[11] J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Analyt.*, 1944, **16**, 111.
[12] P. Job, *Ann. Chim.*, 1928, **9**, 113.
[13] W. C. Vosburgh and G. R. Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437.
[14] A. E. Harvey and D. L. Manning, *ibid.*, 1950, **72**, 4488.
[15] J. Bjerrum, G. Schwarzenbach and L. G. Sillén, *Stability Constants*. Chemical Society (London), 1957. Part I p. 53.
[16] G. H. Morrison and H. Freiser, *Solvent Extraction in Analytical Chemistry*. John Wiley & Sons, New York, 1957.
[17] E. Abrahamczik, *Mikrochem. Mikrochim. Acta*, 1947, **33**, 209.
[18] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, *Applied Inorganic Analysis*. John Wiley & Sons, 2nd Ed., New York, 1953, p. 870.
[19] O. L. Davies (Editor), *Statistical Methods in Research and Production*. Oliver and Boyd, Edinburgh and London, 1947, pp. 99–102.

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THE COULOMETRY AND POLAROGRAPHY OF IRIDIUM^{IV}

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Summary—The coulometric and polarographic behaviour of iridium^{IV} has been investigated. In a 0·2*M* hydrochloric acid electrolyte, at potentials negative enough to prevent the oxidation of the mercury, the iridium gives a diffusion current plateau suitable for polarographic determinations. Electrolysis at a controlled electrode potential shows that the reduction requires one electron per mole, and has been used for the coulometric determination of 3- to 17-mg amounts of iridium. The behaviour of iridium in other electrolytes has also been investigated.

INTRODUCTION

A SURVEY of the literature has revealed no polarographic procedures suitable for the determination of iridium. A recent critical review[1] has discussed the titrimetric methods that have been recorded for iridium, most of which involve the titration of the strongly oxidising iridium^{IV} in acid solution with reducing agents.

In most cases these reductions proceeded smoothly and rapidly at room temperature. The present study shows that the corresponding reduction of iridium can be carried out at a mercury or platinum cathode controlled at a suitable potential, and can be used for a coulometric or polarographic determination of iridium.

EXPERIMENTAL

Apparatus

The controlled-potential coulometric titrations were carried out using an apparatus patterned on that of Kelley, Jones and Fisher.[2] The current integrator was an operational amplifier with capacitance feedback, and the titration output was read and followed on a Brown Instrument 10-mV strip-chart recorder. The titration instrument was calibrated using a 100-ohm standard resistance in place of the cell. The calibration current was calculated from the potential drop across the standard resistance as measured with a potentiometer and standard cell. The output was 0·530 coulombs per mV with a 50-K ohm input resistor and 0·265 coulombs per mV with a 100-K ohm input resistor.

Diaphragm-type cells with mechanical stirring were used for all electrolyses. For titrations employing a platinum electrode (oxidations and reductions), the cell was a 100-ml tall-form beaker, and the electrode was a cylindrical cage, 2·5 cm in diameter, consisting of 7 loops of 1-mm wide platinum foil. The inner compartment, a chamber 1·5 cm in diameter, was separated from the outer cell by an ultrafine fritted-glass disc.

For controlled potential reductions with a mercury cathode an H-type cell was used. The cathode compartment had a volume of 100 ml and the electrode consisted of 20 ml of mercury with a surface area of 16 cm^2. The mercury was introduced into the cell by a bottom stopcock and levelling bulb, but only after de-aeration of the electrolyte was complete. The two compartments of the cell were separated by a coarse fritted-glass disc backed by an agar-potassium chloride gel.

The reference electrode was a Beckman Instruments 5″ external saturated calomel electrode with a fibre-type junction. For the titrations in solutions containing perchlorate, an intermediate bridge containing 1*M* hydrochloric acid was used with the reference electrode. A silver-silver chloride working electrode in 1*M* hydrochloric acid was used in the second compartment in all titrations. Prepurified nitrogen (less than 20 ppm of oxygen) was used to displace the oxygen from the electrolysis solutions.

Polarograms were recorded on a Leeds and Northrup Type E Electrochemograph using a conventional H-type cell with a saturated calomel reference electrode. Absorption spectra were recorded on a Bausch and Lomb Spectronic 505 recording instrument using matched 1-cm quartz cells.

All potentials, in V, are relative to the saturated calomel electrode, unless otherwise noted.

Standard iridium solution

The stock solution was prepared by dissolving 1·90 g of sodium chloroiridate (Johnson, Matthey and Co.) in 2 litres of 0·1*M* hydrochloric acid. The solution was standardised gravimetrically by precipitation of the hydrous oxide using the method of Gilchrist.[3] Three 50-ml aliquots of the solution gave, on ignition in hydrogen, 16·9, 16·9 and 17·2 mg of iridium. Subsequent coulometric titrations of 10-ml aliquots of the solution showed no significant trend over a period of 3 months, indicating that the iridium^{IV} was stable. Other 10-ml aliquots of the solution were added to 80 ml of 0·2*M* hydrochloric acid, heated to 80°, and treated with chlorine for 30 min. The excess chlorine was then removed by boiling, the solution was cooled, and the iridium was determined by coulometric titration. The treatment with chlorine produced no change in the results of the coulometric titration, indicating that the standard solution contained insignificant amounts of iridium^{III}.

Studies in hydrochloric acid

Polarography of iridium^{IV} in 0·2M *hydrochloric acid:* In a 0·2*M* hydrochloric acid supporting electrolyte, iridium^{IV} gives a well defined diffusion current plateau at potentials negative enough to prevent the oxidation of the mercury. The diffusion current was found to be proportional to the concentration of iridium^{IV}, and, at fixed concentration, to the square root of the height of the mercury column of the dropping electrode, indicating a diffusion controlled process (Table I).

TABLE I

	$C_{Ir^{IV}}$, *mM*	i_d*, *μ amp*	i_d*/C	i_d*/Ch½
h 36·0 cm	0·442	1·15	2·60	
m 1·514 mg/sec	0·884	2·29	2·59	
t* 5·34 sec	1·327	3·47	2·61	
		mean	2·60	0·43
h 49·0 cm	0·442	1·33	3·01	
m 2·087 mg/sec	0·884	2·67	3·02	
t* 3·82 sec	1·327	4·03	3·04	
		mean	3·02	0·43

* i_d and t measured at −0·20 V; 25°

Controlled potential electrolysis: Controlled potential reductions of the iridium^{IV} at either a mercury cathode at 0 V or a platinum cathode at 0 or 0·40 V in the 0·2*M* hydrochloric acid electrolyte gave results consistent with a 1 faraday per mole reduction. The potential of an iridium solution after passage of 50% of the total quantity of electricity necessary for the reduction was measured with a platinum indicator electrode and found to be +0·81 V at 25°. This permits the assignment of the formal potential to the couple in 0·2*M* hydrochloric acid:

$$IrCl_6^{2-} + e \rightleftharpoons IrCl_6^{3-}, \quad E^\circ = +1{\cdot}05 \text{ V } vs. \text{ N.H.E.}$$

Quantities of iridium from 3 to 16 mg have been determined by a controlled potential reduction based on an equivalent weight of 192·2 for the iridium (Table II). The titrations were carried out after a pre-electrolysis of the supporting electrolyte. An 80-ml portion of the 0·2*M* hydrochloric acid electrolyte was introduced into the cell, de-aerated, and then reduced at the potential to be used in the subsequent determination. The electrolysis was continued until a negligible residual current was obtained (0·01 mA), then the circuit was interrupted, in the case of mercury the cathode was withdrawn from the cell, and the sample aliquot was added. The titration was not initiated until sufficient time had elapsed for the displacement by the nitrogen of the dissolved oxygen introduced with the sample. Electrolysis for 60 min was generally sufficient to give a quantitative reduction. The current decreased in an exponential fashion to a negligible residue (0·01–0·03 mA).

TABLE II

Reduction	Ir taken, *mg*	Ir found, *mg*
Pt cathode, 0 V	17·0	16·72, 16·66
	8·5	8·34, 8·39
	3·40	3·26, 3·28, 3·32[a]
		3·32, 3·34[a] 3·35
		3·32[b], 3·35[b]
	9·15[c]	9·02, 9·06
	10·3[d]	9·82, 9·85
Pt cathode, 0·40 V	3·40	3·30, 3·36
Hg cathode, 0 V	8·5	8·21, 8·26
	3·40	3·32, 3·31
		3·31[b], 3·31[b]

[a] Ir solution treated with Cl_2 before determination.

[b] Ir reduced at a Pt cathode, 0 V, then reoxidised with Cl_2 before determination.

[c] $(NH_4)_2IrCl_6$ solution standardised against 2-mercaptobenzothiazole[5] (G.G.T.)

[d] Na_2IrCl_6 solution standardised by hydrolytic precipitation (H.I.R.Z.)

The reduced iridium solution could be quantitatively oxidised back to iridium^{IV} by bubbling chlorine through the hot acid solution for 60 min. The excess chlorine could then be removed by gentle boiling for 30 min and the iridium determined by coulometric titration. Boiling of the solution for up to 120 min, maintaining the volume by the addition of water, was found to have no effect on the results of the subsequent titration.

The mean value for the twenty titrations of aliquots of the standard iridium solution was 0·332 mg of iridium per ml, with an average deviation of 0·002 mg. The result differs from the mean value of 0·340 mg per ml obtained by hydrolytic precipitation, but it has been said that this method gives high results.[4]

Attempts to oxidise the reduced iridium solutions at a platinum anode controlled at +1·0 V gave large and steady residual currents (0·3 to 0·5 mA). Subsequent coulometric reduction of these solutions, after boiling to remove any chlorine, gave high results for the iridium.

Studies in perchloric acid

Aliquots of the standard iridium solution were fumed with 10-ml portions of 72% perchloric acid for 30 min, washed down, and again fumed for a further 30 min before dilution to 100 ml. Polarography of the resulting purple solutions gave well defined diffusion current plateaux at potentials negative enough to prevent the oxidation of the mercury. The diffusion current was, in all cases, considerably greater than that in the 0·2*M* hydrochloric acid electrolyte under equivalent conditions, but consistent results could not be obtained. Controlled potential coulometric reductions at a platinum cathode at 0 V were carried out on iridium samples fumed in this fashion. The electrolyses proceeded smoothly with an exponential decay of the current to a small residual value (0·01 to 0·03 mA), but values from 1·39 to 1·76 faradays per mole were obtained in the series of ten reductions.

It would appear that the fuming with perchloric acid gave a partial and variable oxidation of the iridium^{IV} to a higher state. This is in agreement with the results obtained by McBryde and Cluett[6] for the potentiometric titration with iron^{II} or titanium^{III} of iridium fumed in perchloric acid.

Studies in sulphuric acid

Aliquots of the standard iridium solution were fumed with 10-ml portions of concentrated sulphuric acid for 30 min, washed down, and again fumed for a further 30 min before dilution to 100 ml. Polarography of the resulting colourless solutions gave no reduction wave before the discharge of the supporting electrolyte at a potential of −0·75 V. Attempts to oxidise these fumed iridium solutions at a platinum anode at potentials up to +1·0 V gave only the anode reaction corresponding to that of the electrolyte without iridium.

No conclusion can be drawn respecting the oxidation state of the colourless complex in the fumed solution.

Studies in other electrolytes

The polarography of iridium^{IV} was investigated in an electrolyte 1*M* in sodium hydroxide and in an electrolyte 1*M* in ethylenediaminetetra-acetic acid and 1*M* in sodium hydroxide. No reduction waves were obtained, in agreement with the results previously reported by Willis[7] for ammonia, cyanide, ethylenediamine, pyridine and thiocyanate electrolytes. This indicates that in the presence of alkali or other complexing agents the iridium^{IV} either forms a complex that is not reducible at the dropping mercury electrode or the iridium^{IV} is unstable and has undergone spontaneous reduction.

An examination of the absorption spectra gives some indication of the nature of the reaction (Fig. 1). If an iridium^{III} solution prepared by a controlled potential reduction in 0·2*M* hydrochloric acid is made 0·1*M* in excess sodium hydroxide, a spectrum with a peak at 317 mμ immediately develops and is stable on long standing. If an iridium^{IV} solution in 0·2*M* hydrochloric acid is similarly made 0·1*M* in excess sodium hydroxide, the solution immediately turns colourless and then, over a period of 48 hr in the dark, slowly develops a spectrum identical with that of the iridium^{III} solution. The reaction is catalysed by sunlight. The disappearance of the iridium^{IV} can be followed by reacidification of aliquots of the solution at intervals of time. Reacidification of the final solutions with hydrochloric acid gave, in both cases, the colourless solution characteristic of iridium^{III}, and subsequent oxidation with chlorine restored the brown colour of iridium^{IV}.

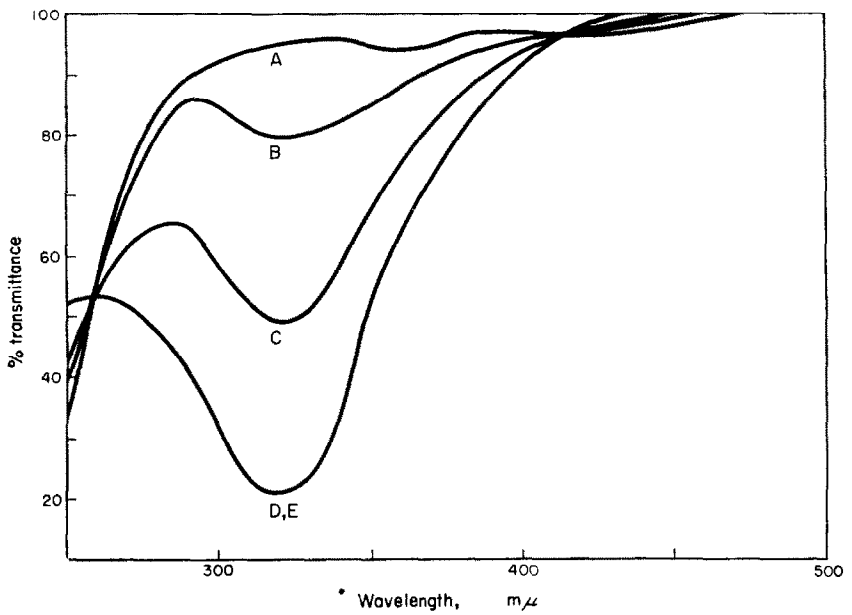


FIG. 1.—Spectrum of 0·30 m*M* iridium solutions in 0·1*M* excess sodium hydroxide:
Ir^{IV}: A, on mixing; B, 2 hr; C, 8 hr; D, 48 hr standing
Ir^{III}: E, on mixing.

A similar reaction was found to take place in the 1*M* ethylenediaminetetra-acetic acid plus 1*M* sodium hydroxide electrolyte, except that the absorption peak was shifted to 315 mμ. This peak is the basis of the spectrophotometric determination of iridium^{IV} proposed by MacNevin and Kriege.[8]

It would appear that the iridium^{IV} is reduced to iridium^{III} in the basic solutions. However, the immediate disappearance of the polarographic wave in basic solution contrasts with the slow appearance of the iridium^{III} spectrum in the air-saturated solutions. It would appear that the iridium^{IV} complex in basic solution does not react at the dropping mercury electrode at any appreciable rate.

DISCUSSION

Polarography in 0·2*M* hydrochloric acid provides a means for the relative assay of pure iridium^{IV} solutions. The method must be standardised against solutions of known iridium content. Coulometry in the 0·2*M* hydrochloric acid electrolyte provides a means for the absolute assay of a pure iridium^{IV} solution. The method is standardised by reference to a standard cell and a standard resistance.

Application of these methods to the determination of iridium in a general scheme of analysis would depend greatly on the nature of the sample. Reference to the standard potentials of the appropriate couples,[9] indicates that gold^{III}, palladium^{II}, platinum^{IV} and rhodium^{III}, amongst others, would be expected to interfere. The degree of complexity of the equilibria of these metals in mineral acid solution is such however, that specific solution preparations might give no interference.

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Zusammenfassung—Das coulometrische und polarographische Verhalten von Iridium(IV) wurden untersucht. In 0,2 m Salzsäure als Elektrolyt ist das Potential genügend negativ um eine Oxydation von Quecksilber auszuschalten. Iridium zeigt ein Plateau in der Strom-Spannungskurve, welches geeignet für polarographische Bestimmungen ist. Elektrolyse mit kontrolliertem potential zeigt, dass ein Elektron zur Reduktion nötig ist. Die coulometrische Bestimmung von 3–17 mg Iridium wurde elfolgreich druchgeführt. Das Verhalten von Iridium in anderen Elektrolyten wurde ebenfalls studiert.

Résumé—L'auteur a étudié le comportement coulométrique et polarographique de l'iridium(IV). En milieu acide chlorhydrique 0,2*M*, à des potentiels suffisamment négatifs pour empêcher l'oxydation du mercure, l'iridium donne une vague de diffusion convenable pour des dosages polarographiques. L'électrolyse à potentiel contrôlé montre que la réduction nécessite un électron par mole; elle a été utilisée pour le dosage coulométrique de 3 à 17 mg d'iridium.

Le comportement de l'iridium dans d'autres électrolytes a aussi été étudié.

REFERENCES

[1] F. E. Beamish, *Analyt. Chim. Acta.*, 1959, **20,** 101.
[2] M. T. Kelley, H. C. Jones and D. J. Fisher, *Analyt. Chem.*, 1959, **31,** 488.
[3] R. Gilchrist, *J. Res. Nat. Bur. Stand.*, 1932, **9,** 547.
[4] M. A. Hill and F. E. Beamish, *Analyt. Chem.*, 1950, **22,** 590.
[5] R. R. Barefoot, W. J. McDonnell and F. E. Beamish, *ibid.*, 1951, **23,** 514.
[6] W. A. E. McBryde and M. L. Cluett, *Canad. J. Res.*, 1950, **28B,** 788.
[7] J. B. Willis, *J. Amer. Chem. Soc.*, 1944, **66,** 1067.
[8] W. M. MacNevin and O. H. Kriege, *Analyt. Chem.*, 1956, **28,** 16.
[9] W. Latimer, *Oxidation Potentials.* Prentice-Hall Inc., New York, 2nd edition, 1952.

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MIXED CHEMILUMINESCENT INDICATORS

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Summary—A 1 : 1 molar mixture of luminol and fluorescein in the presence of hydrogen peroxide has been shown to be a sensitive and reversible chemiluminescent indicator for acid-base titrations. The role played by the fluorescein and luminol is discussed.

THE use of chemiluminescent indicators in titrimetric analysis has been thoroughly investigated by Erdey and coworkers and the results have been summarised.[1]

For acid-base titrations, the indicators lucigenin, luminol and lophine have been used. Lucigenin is the most satisfactory since no catalysts are required and the indicating reaction is reversible. The intensity of chemiluminescence is less than that obtained from catalysed luminol solutions but luminol is irreversibly destroyed in alkaline solution and accordingly is only recommended for the titration of acids with bases.

We have observed that the intensity of lucigenin chemiluminescence can be markedly increased by adding fluorescein. A similar increase was observed on mixing fluorescein and luminol and, as described in this paper, this mixture has proved to be useful as a reversible indicator for acid-base titrations. The effect of fluorescein is discussed in this paper and an indicator reaction mechanism proposed. Further studies are being made of the behaviour of other materials which fluoresce strongly.

EXPERIMENTAL

Effect of fluorescein on chemiluminescence

Either 1 ml of 0·2% lucigenin solution or 1 ml of 0·1% luminol solution was added to 10-ml aliquots of 0·01*N* sodium hydroxide solution containing 1 ml of 6% H_2O_2, and these alkaline peroxide solutions were heated to *ca.* 60°. To each aliquot, a volume (0–5 ml) of 0·25% sodium fluoresceinate was added.

In the absence of fluorescein, the heated alkaline solutions emitted greenish-white light on the addition of lucigenin and pale blue chemiluminescence on the addition of luminol. On the inclusion of increasing amounts of fluorescein in the solutions, the emitted light increased in intensity and finally had the characteristic bright green colour observed during the fluorescence of fluorescein. The intensity increased with increasing concentration of fluorescein up to the point where the fluorescein concentration was approximately double the concentration of luminol present. With higher concentrations of fluorescein the intensity decreased from this maximum because of self-absorption by the dye molecules.

When solutions containing luminol were cooled the colour faded rapidly, the rate of fading decreasing with increasing concentration of fluorescein present.

In another series, the fluorescein content was kept constant and the luminol content varied. In these tests, a marked increase in chemiluminescence intensity occurred on increasing the amount of luminol present up to approximately half the percentage composition of fluorescein present, but no significant increase resulted from adding larger volumes.

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The most suitable mixture for use as an indicator was thus found to be a combination of equal volumes of 0·1 % luminol and 0·25 % fluorescein, *i.e.* about a 1 : 1 molar mixture. Decreasing volumes of this mixed indicator solution were then added to hot alkaline peroxide solutions to determine the sensitivity of the indicator. In the presence of 1 ml of indicator per 20 ml of solution, chemiluminescence of moderate intensity was retained even on cooling. Provided the alkaline solutions were maintained hot, a pale chemiluminescence was obtained in the presence of 0·01 ml of indicator per 20 ml of solution and the light was just discernible if this amount of indicator was halved.

Titrations using fluorescein-luminol mixed indicator

The mixed indicator solution was prepared by dissolving 0·25 g of fluorescein and 0·1 g of luminol in 10 ml of 0·1*N* sodium hydroxide solution and diluting to 100 ml.

One ml of 6 % H_2O_2 and 1 ml of indicator solution were added to 20·00-ml aliquots of standard hydrochloric acid solutions. The solutions were heated to 60° and titrated in the dark with standard sodium hydroxide solution to the appearance of permanent chemiluminescence. Measurements with a pH meter showed that this chemiluminescence appeared at a pH of 8·9. Excess base was then added, and the solution back-titrated with acid to the disappearance of light. In another series, the starting point was 20·00-ml aliquots of standard sodium hydroxide solution. The results are summarised in Table I.

TABLE I.—ACID-BASE TITRATIONS

Titrant	Mean of ten titrations, *ml*	Precision (standard deviation)		Deviation from phenolphthalein, %
		ml	%	
1*N* NaOH	19·97	±0·04	±0·20	0·15
0·1*N* NaOH	20·05	±0·07	±0·35	0·20
0·01*N* NaOH	20·90	±0·17	±0·85	0·50
1*N* HCl	19·97	±0·04	±0·20	0·15
0·1*N* HCl	19·83*	±0·06	±0·30	0·40
0·01*N* HCl	18·11*	±0·26	±1·45	1·00

* Low values because of the presence of 5×10^{-4} moles of Na_2CO_3 per litre of NaOH.

Since the peroxide solution had a slight acidity and the indicator a slight alkalinity, it was necessary to determine a reagent blank by taking 5 ml of indicator and 5 ml of 6 % H_2O_2 in 20 ml of hot water and titrating with standard base (preferably 0·01*N*) to the appearance of light. In the above titrations, the indicator plus peroxide blank amounted to 0·40 ml of 0·01*N* sodium hydroxide solution and this correction was applied to all direct titration values.

To test the suitability of the indicator for micro-titrations 5-ml aliquots of 0·1*N* solutions of acetic, citric, oxalic and tartaric acids were titrated with 0·1*N* sodium hydroxide solution using 1 ml of 6 % H_2O_2 and 1 ml of mixed indicator per aliquot. The titrations were repeated using phenolphthalein as indicator and the results are compared in Table II. It can be seen from this table and from the

TABLE II.—TITRATION OF 5·00 ml OF 0·1*N* WEAK ACID SOLUTIONS WITH 0·1*N* SODIUM HYDROXIDE SOLUTION

Acid	Mean of six titrations		Deviation between the two results, %
	Phenolphthalein, *ml*	Luminol-fluorescein, *ml*	
Acetic	4·97	4·99	0·4
Citric	4·95	5·24*	6·0
Oxalic	4·99	4·97	0·4
Tartaric	4·98	4·97	0·2

* Indistinct end-point; chemiluminescence masked.

deviations noted in Table I that, with the exception of the titration of citric acid, the mixed indicator gave similar titration values to those obtained using phenolphthalein indicator.

The indicator proved to be completely reversible provided that the titrations were commenced at *ca.* 60°. Similar titres were obtained in direct titrations and in back titrations and the precision values quoted in Table I are derived from the values obtained in both ways. It was possible to titrate a solution back and forth at least six times without any further addition of indicator.

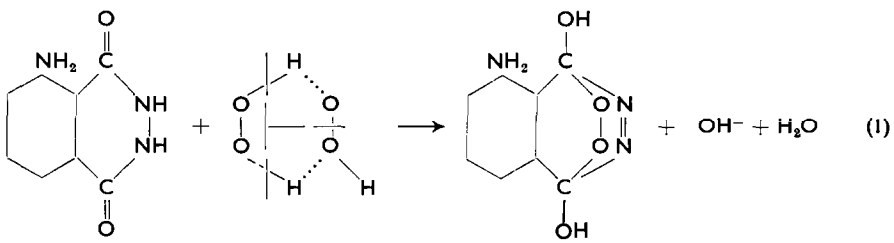
Some warning of the approach of the equivalence point was obtained with this indicator. In titrations with alkali, the duration of the flashes of light obtained on the addition of drops of titrant increased near the equivalence point. When titrating with acid solutions, there was a dimming of the chemiluminescence before complete extinction. Greater sensitivity was obtained by shaking the solutions vigorously at this stage of the titration.

DISCUSSION

In the original study of the use of luminol as an acid-base indicator, Kenny and Kurtz[2] used 40 mg of luminol and 30 mg of haemin catalyst per titration and the indicator reaction was irreversible. In the present study only 1 mg of luminol and 2·5 mg of fluoroscein were used per titration, the indicator reaction proved reversible, and the precision obtained was equivalent to that recorded in earlier studies. A similar saving in indicator material may be obtained using lucigenin since the presence of fluorescein greatly enhances the intensity of the emitted light.

The role played by fluorescein in these mixed indicators requires some explanation. Fluorescein, eosin and rhodamine chemiluminesce with a colour tone resembling fluorescence when oxidised with hydrogen peroxide in sodium hydroxide solution, the intensity of the chemiluminescence increasing with temperature and with increasing concentrations of alkali, dye and hydrogen peroxide.[3] With the concentrations of reactants used in this study, only very weak emissions are observed unless luminol is added. If the luminol is destroyed by adding other catalysts, such as haemin or heavy metal ions, there is a marked increase in brilliance as the luminol reacts with these catalysts, then the solution reverts to the pale luminescence of the fluorescein or eosin present. The intensity can be restored by adding further luminol. It can, therefore, be suggested that luminol is acting as a catalyst for the chemiluminescent reaction of xanthene dyes.

In the mechanisms proposed to explain the chemiluminescence of lucigenin and luminol, the primary step is envisaged as the formation of a trans-annular peroxide.[1] With hydrogen peroxide as the oxidising agent, the reaction with luminol can be written as follows:



(I)

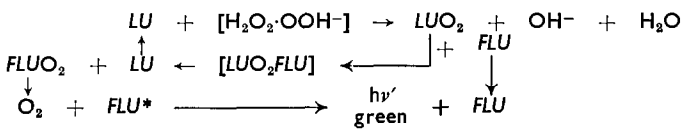
Hydrogen peroxide can exist in several forms in aqueous solution depending on the pH of the solution. At pH < 12, the hydrogen peroxide is present mainly as molecular H_2O_2. On increasing the pH, perhydroxyl ions are formed in the solution and react with excess H_2O_2 to give the ion $H_2O_2 \cdot OOH^-$, which reaches a maximum

concentration at pH 12.[4,5] Above pH 12 the concentration of perhydroxyl ions increases and at pH 14 the species present is mainly the perhydroxyl ion. In the mixed indicator, a maximum emission of light was observed at pH *ca.* 12 so that the preferred species of hydrogen peroxide for the oxidation must be $H_2O_2 \cdot OOH^-$ as shown in equation (1).

The reaction of hydrogen peroxide with lucigenin, eosin, fluorescein, *etc.* can be written in an analogous manner.

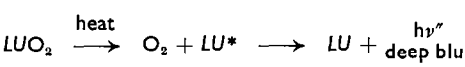
The formation of the trans-annular peroxide compound facilitates singlet-triplet conversion within the molecule through the triplet state or magnetic field associated with the oxygen. If the peroxide now be decomposed, the remaining molecule is left in an excited, unstable triplet state which reverts to the singlet state with the emission of light.

The luminol can catalyse the chemiluminescence of fluorescein by facilitating the formation of fluorescein peroxide through formation of a transitional complex and oxygen transfer. Using *LU* and *FLU* as abbreviations for luminol and fluorescein, respectively, the light producing mechanism can be summarised as follows:



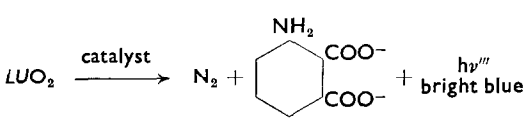
(2)

In the absence of fluorescein or catalysts, the LUO_2 can be decomposed by heat, but this reaction is slow:



(3)

In the presence of catalysts such as haemin and heavy metal ions, luminol is irreversibly oxidised by a different mechanism and yields the following products:[1]



(4)

The role of luminol in reaction (2) is similar to the role played by sensitisers in the photo-oxidation of organic compounds, and it is interesting to note that eosin has been widely used as a sensitiser for the preparation of the trans-annular peroxides of a number of steroids and linear polyacene aromatic hydrocarbons.[6] In these preparations, the role of the sensitiser is that of a carrier of reactive oxygen to the substrate, thus allowing the oxidation to proceed by a considerably lowered barrier.

It is possible to suggest an alternative mechanism in which fluorescein can be regarded as a catalyst for the decomposition of the luminol peroxide, resulting in an increased yield of the deep blue light observed on thermal decomposition [*cf.* equation (3)]. These radiations can then be presumed to activate the fluorescein and result in a green fluorescence. This mechanism was not supported by experimental evidence, for no green fluorescence was observed when luminol, chemiluminescing from thermal decomposition, was separated by a glass wall from alkaline fluorescein solution, but mixing of the two solutions yielded bright green light immediately. Collision of the two molecules must therefore be an integral part of the mechanism.

A similar set of equations can be written to explain the behaviour of lucigenin–fluorescein mixtures.

On the basis of the proposed mechanism, a number of fluorescent materials could be sensitised. In this way it should be possible to develop a series of mixed chemiluminescent indicators which would be useful for a variety of titrations.

Acknowledgements—Two of us (L. E. and W. F. P.) wish to acknowledge Research Fellowships from the Queen's University, Belfast, which made participation in this project possible.

Zusammenfassung—Eine 1:1 (Molbasis) Mischung von Luminol und Fluorescein ist in Gegenwart von Wasserstoffperoxyd ein empfindlicher und reversibler Chemiluminiszenzindicator für Säure-Basentitrationen. Die Wirkung der beiden Substanzen wird diskutiert.

Résumé—Les auteurs ont montré qu'un mélange mole à mole de luminol et de fluorescéine était un indicateur chimioluminescent sensible et réversible pour les titrages acide-base. Le röle joué par la fluorescéine et le luminol est discuté.

REFERENCES

[1] L. Erdey, *Ind. Chemist.*, 1957, **33**, 459, 523 and 575.
[2] F. Kenny and R. B. Kurtz, *Analyt. chim.*, 1951, **23**, 339.
[3] R. Twaki, *Nippon Kogaku Zasshi*, 1957, **78**, 1613; *Chem. Abs.*, 1958, **51**, 5140.
[4] L. Erdey, *Acta Chim. Hung.*, 1953, **3**, 105.
[5] F. R. Duke and T. W. Haas, *J. Phys. Chem.*, 1961, **65**, 304.
[6] C. Reid, *Quart. Revs.*, 1958, **12**, 205.

Talanta, 1962, Vol. 9, pp. 377 to 386. Pergamon Press Ltd. Printed in Northern Ireland

IMPROVED PYROGALLOL DETERMINATION OF NIOBIUM BASED UPON EXTRACTION OF A QUATERNARY AMMONIUM ION COMPLEX

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Summary—The optical absorbance produced by mixing niobium^{V} with pyrogallol in a slightly alkaline solution is increased approximately 60% by the presence of a long-chain quaternary ammonium compound. In addition, the interferences from molybdenum^{VI}, tungsten^{VI} and chromium^{VI} can be virtually eliminated and that from vanadium^{V} halved by an extraction of the niobium complex with ethyl acetate. Tantalum accompanies niobium but, by selection of the wavelength, interference from moderate amounts can be minimised. Interference by titanium is very serious but somewhat less than in the original procedure of Hunt and Wells.

INTRODUCTION

As the result of a study on the enrichment and eventual separation of niobium and tantalum by foam fractionation, a reliable and simple method was required to determine each of these elements in the presence of the long-chain quaternary ammonium salt used as the foam-producing agent. Among the available methods for niobium, one using pyrogallol[23] was preferred to the others, mainly because of the possibility of applying it to dilute aqueous solution without further preparation and because the same reagent could be used, under different conditions, for tantalum. In contrast, the peroxy method requires one to work with fairly concentrated sulphuric acid, and its sensitivity is rather poor.[4,6,14,22,29,30] The thiocyanate approach is still subject to a series of interferences and, in addition, uses a very volatile solvent (ethyl ether) in its most sensitive modification.[2,3,11,13,31] Finally, the hydroquinone procedure is quite sensitive to temperature.[8,13,19]

Successive modifications and improvements of the pyrogallol method have been reported and reviewed in detail by different authors.[5,7,12,32,33] The Hunt and Wells technique[12] was chosen among them as a basis for our study because of its relative simplicity.

The present study shows that the sensitivity of the Hunt and Wells procedure[12] is nearly doubled in the presence of a long-chain tetra-alkylammonium salt, and that the specificity of the procedure can be markedly improved by extraction with ethyl acetate.

EXPERIMENTAL

Reagents

Salt mixture: A solution to simulate a typical one in which niobium might be found after fusions of an ore or alloy was made up to contain sulphate, oxalate and citrate. Citrate was present as well as oxalate to form soluble complexes and also because the oxalate was much less soluble than citrate. One litre of solution containing 62·5 g of $Na_2SO_4 \cdot 10\ H_2O$ and 62·5 g of $(NH_4)_2HC_6H_5O_7$ was mixed with an equal volume of 4% ammonium oxalate solution.

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Test solutions: Stock solutions ($1 \times 10^{-2}M$) of niobium^{V} and tantalum^{V} were prepared by dissolving an appropriate amount of the metal in a platinum dish using 10 ml of 48% hydrofluoric acid plus a few drops of concentrated nitric acid. After evaporation on a steam bath to about 5 ml, the solution was made up to 1 litre. The diluent for niobium was 4% ammonium oxalate solution; that for tantalum was the salt mixture.

Titanium^{IV} was prepared in the same way as the tantalum except that TiO_2 was used as the starting material. The $0{\cdot}5M$ solutions of tungsten^{VI}, molybdenum^{VI}, vanadium^{V}, and phosphate were prepared by dissolving $Na_2WO_4{\cdot}2\,H_2O$, $Na_2MoO_4{\cdot}2\,H_2O$, $Na_3VO_4{\cdot}16\,H_2O$, and $Na_2HPO_4{\cdot}7\,H_2O$ in distilled water. The vanadate solution had to be filtered to remove a slight turbidity; further dilutions, $5{\cdot}0 \times 10^{-2}M$ and $5{\cdot}0 \times 10^{-3}M$, were prepared with 4% ammonium oxalate solution, except for vanadate and tungstate which had to be diluted with water.

The $0{\cdot}5M$ solutions of chromium^{VI} and fluoride were prepared from $Na_2CrO_4{\cdot}4\,H_2O$ and NaF using 4% ammonium oxalate solution as solvent. Another fluoride solution was prepared in water.

Sodium bisulphate solution, 9% aqueous: This was substituted for the potassium salt in the Hunt and Wells procedure[12] to minimise the potassium content.

Ethoquad 18/25 (polyethoxy-15-stearyl-methylammonium chloride) solution, $0{\cdot}001M$: Prepared by diluting 1 g to 1 litre with salt mixture (or with 4% ammonium oxalate solution or with water in certain cases).

Pyrogallol reagent: Immediately before use dissolve 4 g of pyrogallol in 120 ml of 10% anhydrous sodium sulphite and dilute to 200 ml.

Wash solution: Ethyl acetate extracts were washed with portions of a mixture prepared from 80 ml of 10% sodium sulphite plus 80 ml of $0{\cdot}001M$ Ethoquad (in salt solution) diluted to 200 ml.

Apparatus

Spectrophotometric measurements were made with a Beckman DU instrument equipped with silica cells. pH measurements were made with a glass electrode connected to a Beckman Zeromatic pH meter.

Procedure

The adopted technique ensures that the concentrations of reagents in the aqueous sample are 2·5% citrate, 2·5 sulphate, 2·4% sulphite, 0·48% oxalate, $4{\cdot}0 \times 10^{-4}M$ Ethoquad, and 0·8% pyrogallol The pH is $7{\cdot}5 \pm 0{\cdot}1$. These conditions are attained by adding to a sample 20 ml of Ethoquad reagent (in salt mixture), 5 ml of $1M$ sodium hydroxide, 20 ml of pyrogallol reagent, and diluting to 50 ml with water.

The absorbance of the above mixture can be measured at 410 mμ against a similar blank to determine niobium with little interference from tantalum, but extraction into ethyl acetate is preferred for better selectivity even though the sensitivity is slightly less. Extraction of a 25-ml aliquot of sample is performed in a 125-ml separatory funnel of the Squibb type. Successively, 10-, 5- and 5-ml portions of ethyl acetate are shaken vigorously for 2 min each. The collected extracts are then washed three times with 5-ml portions of wash solution and, finally, filtered into a 25-ml calibrated flask through about 8 g of anhydrous sodium sulphite. The latter serves to dry the extract and simultaneously prevent its oxidation. The extract is diluted to volume and the absorbance at 410 mμ measured against an ethyl acetate blank.

RESULTS

Preliminary work

Niobium and pyrogallol are reported[16] to form a 1:1 complex in aqueous solution. However, it has been confirmed that a large excess of pyrogallol is required to attain a maximum absorbance, a situation similar to that reported for the titanium complex.[28] Under Hunt and Wells's conditions[12] the presence of Ethoquad enhanced the absorption without shifting the peak at 358 mμ (Fig. 1). The absorption value was independent of the order of mixing the reagents. By adding increasing amounts of Ethoquad to a solution containing $4{\cdot}0 \times 10^{-5}M$ niobium and 0·8% pyrogallol, a combining ratio of 2 niobium to 5 Ethoquad was found.

A quick survey of other quaternary ammonium compounds showed that neither tetramethylammonium chloride nor benzyltrimethylammonium chloride enhanced the niobium-pyrogallol colour. Tribenzylamine and lauryltrimethylammonium chloride produced precipitates. The lauryl derivative extracted to give a spectrum

(Fig. 2) which had an absorbance at 410 mμ somewhat less than that for the aqueous Ethoquad system, and it was linear with niobium concentration. Furthermore, a large excess of the lauryl compound is necessary to attain a maximum absorbance. Extrapolation led to a combining ratio of 1 niobium to 5 lauryltrimethylammonium ions.

Extractability of the lauryl derivative prompted two further tests. In one, the failure of the niobium-pyrogallol complex to extract with ethyl acetate in the absence

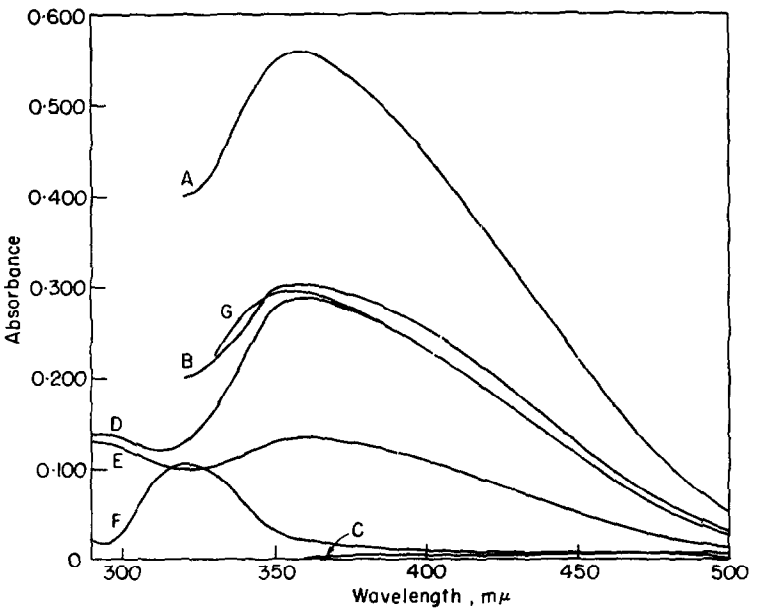


FIG. 1.—Niobium spectra showing the effects of Ethoquad and the chosen salt mixture:
Series 1 [0·8%(6·4 × $10^{-3}M$) pyrogallol]:
A—4·0 × $10^{-5}M$ Nb, 2·0 × $10^{-4}M$ Ethoquad,
B—4·0 × $10^{-5}M$ Nb,
C—2·0 × $10^{-4}M$ Ethoquad.
Series 2 [0·8% pyrogallol, 0·48%$(NH_4)_2C_2O_4 \cdot H_2O$, 2·4% Na_2SO_3, 2·5% $Na_2SO_4 \cdot 10\ H_2O$, 2·5% $(NH_4)_2HC_6H_5O_7$]:
D—2·0 × $10^{-5}M$ Nb, 4·0 × $10^{-4}M$ Ethoquad,
E—2·0 × $10^{-5}M$ Nb,
F—4·0 × $10^{-4}M$ Ethoquad,
G—same as D but 5 ml of 1M NaOH per 50 ml of solution present (final pH 7·5 – 7·6).

of the quaternary ammonium ion was demonstrated over a wide range of pH. This agrees with a very recent report[17] which tested a few simple alkyl derivatives. In the second, the Ethoquad complex was shown to extract to give a somewhat lower absorbance than the lauryl extract, but linear over a much larger range.

Comparative absorbance values for several modified procedures are given in Table I.

A brief study of the effect of pH on absorbance showed that an aqueous sample containing niobium-pyrogallol and Ethoquad changed less than one without Ethoquad. Within the pH range 6·4 to 8·4, the absorbance for the former went from 0·287 through a maximum of 0·333, whereas the corresponding values for the Hunt and Wells method were 0·133 and 0·211.

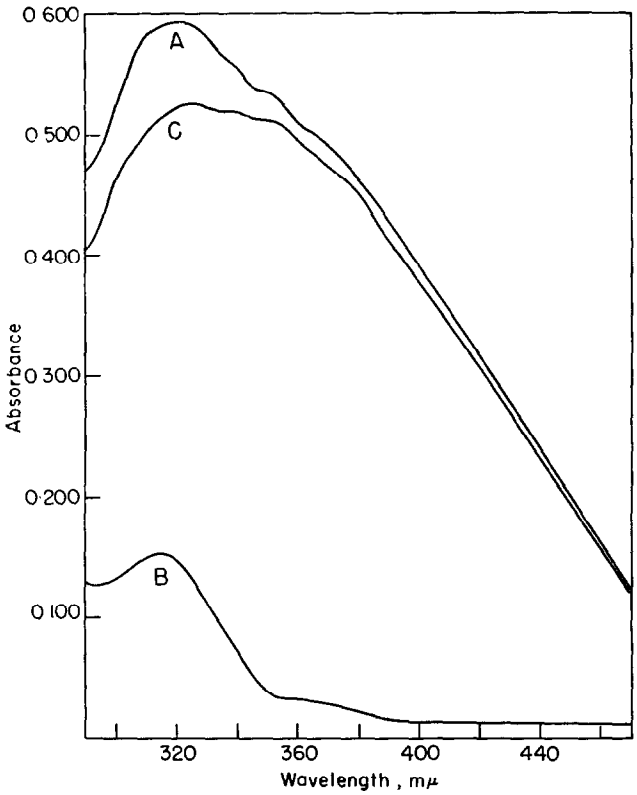


FIG. 2.—Spectra for ethyl acetate extracts of the system niobium – 0·8% pyrogallol-lauryltrimethylammonium chloride (LTMAC) and a blank:
A—$4{\cdot}0 \times 10^{-5}M$ Nb, $2{\cdot}0 \times 10^{-4}M$ LTMAC,
B—$4{\cdot}0 \times 10^{-4}M$ LTMAC,
C—differential curve (A – B/2).

TABLE I.—COMPARATIVE ABSORBANCE VALUES FOR $4{\cdot}0 \times 10^{-5}M$ NIOBIUM USING THE ORIGINAL AND THE MODIFIED HUNT AND WELLS TECHNIQUES

Salt system	Tetra-alkyl ammonium ion ($4{\cdot}0 \times 10^{-4}M$)	Absorbance	
		Direct aqueous solution	Extract
Original	None	0·248	—
Original	Ethoquad	0·404	—
Original	Ethoquad	—	0·349[a]
Original	LTMAC[b]	—	0·399[c]
Proposed	Ethoquad	0·410	—
Proposed	Ethoquad	—	0·352[a]

[a] Washed with three 5-ml portions of washing solution
[b] Lauryltrimethylammonium chloride
[c] Not washed

The composition of the "salt mixture" added to the samples is not critical; it was decided upon in the following way. Because 4% ammonium oxalate solution is close to saturation and because higher concentrations would be required to hold large amounts of tantalum in solution, citrate was added as a supplement. Sulphate was added not only to stimulate the composition from a sample from an ore that had been fused with pyrosulphate but also to improve the extraction by salting out. Sodium salts were preferred to potassium salts which would precipitate potassium fluotantalate.

TABLE II.—INTERFERENCES, IN TERMS OF NIOBIUM, FROM 1 MILLIMOLE OR 1 mg OF CERTAIN METAL IONS

Ion	Concn. units	I Hunt and Wells technique[12]	II Ethoquad added: Aqueous	III Ethoquad added: Extract
Ta^{V}	mmoles	0·043	0·027	0·031
	mg	0·022	0·013	0·015
Mo^{VI}	mmoles	0·48	0·46	0·000
	mg	0·44	0·42	0·000
W^{VI}	mmoles	0·085	0·10	0·000
	mg	0·042	0·05	0·000
V^{V}	mmoles	no value	0·50	0·026
	mg	no value	0·90	0·047
Cr^{VI}	mmoles	not mentioned	0·009	0·000
	mg	not mentioned	0·016	0·000
Ti^{IV}	mmoles	1·09	0·96	0·77
	mg	2·11	1·85	1·49

Extraction variables

Extraction of a 25-ml aqueous sample with successive 10-, 5- and 5-ml portions of ethyl acetate removed 96% of the niobium. The last 5-ml extract contained about 3·5% of the final total.

When the extract was contacted with three 5-ml portions of wash solution, a relative loss of less than 3% was measured. As will be shown later, this loss in sensitivity for niobium is insignificant compared to the gain in selectivity afforded by the washing procedure.

Interferences

It is well known that ions of most of the elements in Groups VA and VIA interfere. Spectra for the aqueous solutions of niobium and six elements are shown in Fig. 3. The interference of each ion in terms of a unit of niobium is shown in Table II for comparison with counterparts in the original Hunt and Wells procedure.[12] In general, the figures are quite similar. However, the last column of the table together with Fig. 4 shows the striking benefits of the extraction step. Although tantalum is perhaps the most likely interference, it seems advantageous to discuss it after the other ions.

Molybdenum^{VI}. Molybdate produces an intense colour with pyrogallol in acetic acid[21] as well as in alkaline media. A combining ratio of 1 molybdate to 2 pyrogallol has been assigned to the complex between pH 6·0 and 8·0.[25] Neither the shape nor the intensity of the spectrum is affected by Ethoquad. Furthermore, it remains non-extractable. Molybdate at 100 times the concentration of niobium does not give a

measurable interference. However, it was found that the absorbance at 355 mμ in the aqueous phase varies linearly with the concentration in the tested range from $2{\cdot}0 \times 10^{-5}$ to $2{\cdot}0 \times 10^{-4}M$, contrary to an earlier report,[20] even though pH 7·5 may not be the most favourable.[1] Up to $4{\cdot}0 \times 10^{-2}M$, neither phosphate nor fluoride affected the reaction.

Tungsten^{VI}. Between pH 6·0 and 8·0, a coloured species has been assigned a 1 tungstate to 2 pyrogallol ratio.[25] Ethoquad does not affect the spectrum. In addition,

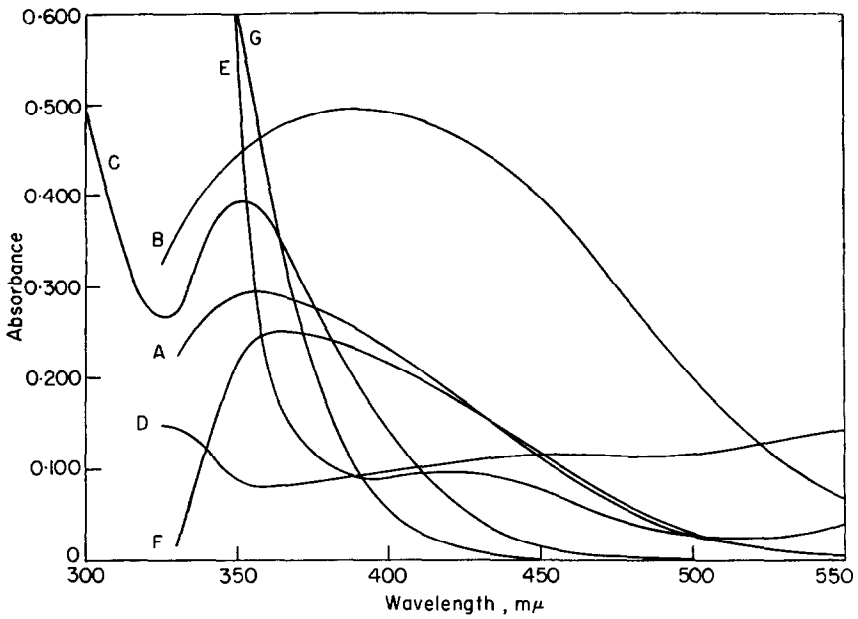


FIG. 3.—Spectra for ions in aqueous solutions prepared by the recommended procedure:
A—$2{\cdot}0 \times 10^{-5}M$ Nb,
B—$1{\cdot}0 \times 10^{-4}M$ Mo,
C—$1{\cdot}0 \times 10^{-4}M$ W,
D—$2{\cdot}0 \times 10^{-5}M$ V,
E—$1{\cdot}0 \times 10^{-3}M$ Cr,
F—$2{\cdot}0 \times 10^{-5}M$ Ti,
G—$1{\cdot}0 \times 10^{-4}M$ Ta.

fluoride and phosphate up to $4{\cdot}0 \times 10^{-2}M$ did not affect the absorbance. At higher concentrations, they helped to retain tungsten in the aqueous phase so that fewer washings were required.

Vanadium.^{V} Vanadate turns yellow upon acidification, but the addition of the alkaline pyrogallol reagent gives a transient purple followed rapidly by the intensely blue reduced species[18] for which the absorption peak falls beyond 800 mμ.[20] Interference is decreased by the extraction step, but it is still serious.

In an effort to reduce the interference, the reduction, extraction and washing steps were examined further. Pyrogallol, in the absence of sulphite, reduced vanadate in neutral and alkaline solutions. Ethyl acetate does not extract the reduced form, but it does extract the yellow form, the amount falling off in both acidic and alkaline media.

Vanadate cannot be extracted by ethyl acetate in the presence of Ethoquad alone, but the reduced species produced by pyrogallol is extractable on adding Ethoquad.

The presence of fluoride, phosphate, arsenate, silicate, cyanide or EDTA was not effective in avoiding reduction or in washing the reduced species (in the presence of Ethoquad) out of the extract. In fact, fluoride and phosphate did not affect the extraction significantly.

As a substitute for ethyl acetate, cyclohexane, ethyl ether, dioxane, tetrahydrofuran,

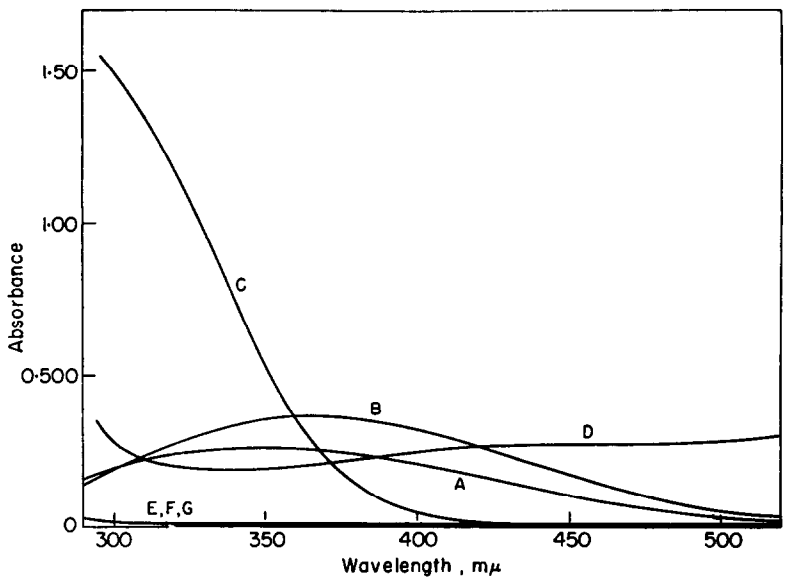


FIG. 4.—Spectra for ethyl acetate extracts obtained by the recommended procedure (extracts were dried but not washed):
A—$2{\cdot}0 \times 10^{-5}M$ Nb,
B—$4{\cdot}0 \times 10^{-5}M$ Ti,
C—$1{\cdot}0 \times 10^{-4}M$ Ta,
D—$1{\cdot}0 \times 10^{-3}M$ V,
E—$2{\cdot}0 \times 10^{-3}M$ Mo,
F—$2{\cdot}0 \times 10^{-3}M$ W,
G—$2{\cdot}0 \times 10^{-3}M$ Cr.

dimethylformamide, di-isobutyl ketone and methyl ethyl ketone were tested. Only methyl ethyl ketone showed sufficient promise to warrant future attention.

It should be mentioned that the extracted blue colour is stable for at least 2 hr and is suitable for quantitative measurement at 410 mμ and, presumably, also above 800 mμ. After 1–2 days, a brown residue forms and the supernate is brown-yellow.

Chromium.[VI] Within a few min after the addition of pyrogallol, the emerald-green reduced species is formed. Fortunately, the species is not extracted.

Titanium.[IV] The yellow colour formed with pyrogallol has long been known.[9,10,24,27] Unfortunately, it is extracted in the presence of Ethoquad. Up to $4{\cdot}0 \times 10^{-2}M$, fluoride and phosphate had no effect. Furthermore, the extract appeared to saturate, the intensity tended to level off above $2{\cdot}0 \times 10^{-4}M$, so that the extract was unsuitable for the quantitative determination of titanium above that concentration.

Tantalum.[V] Although tantalum is often reported not to interfere with niobium determinations, it is clear from Figs. 3 and 4 that the extent of interference depends

greatly upon wavelength. The interference was unaffected by $4{\cdot}0 \times 10^{-3}M$ fluoride in excess. Using the prescribed salt mixture, at $2{\cdot}0 \times 10^{-4}M$ tantalum the aqueous solution is turbid in spite of the citrate and oxalate concentrations; the precipitate formed by $4{\cdot}0 \times 10^{-4}M$ tantalum can be dissolved by contact with $4{\cdot}0 \times 10^{-2}M$ fluoride only if allowed to stand overnight.

TABLE III.—EFFECT OF TANTALUM ON THE DETERMINATION OF NIOBIUM USING THE EXTRACTION PROCEDURE

Niobium, *M*	Tantalum, *M*	Molar ratio of Ta:Nb	Relative Errors, %	
			Direct	Corrected
$2{\cdot}0 \times 10^{-5}$	$1{\cdot}0 \times 10^{-4}$	5	+12·5	+2·3
$2{\cdot}0 \times 10^{-5}$	$2{\cdot}0 \times 10^{-4}$	10	−6·9	−27·7
$2{\cdot}0 \times 10^{-5}$	$3{\cdot}0 \times 10^{-4}$	15	−38·1	−65·3
$2{\cdot}0 \times 10^{-5}$	$4{\cdot}0 \times 10^{-4}$	20	−62·5	

[a] Absorption from tantalum deducted.

Table III, which contains typical data for mixtures of niobium and tantalum, shows that the presence of tantalum leads to a negative error, particularly if the absorbance is corrected for the expected contribution from tantalum. Because the aqueous phase after extraction was clear, adsorption losses were not the cause. By measuring a

TABLE IV.—EFFECT OF PYROGALLOL CONCENTRATION ON THE INTERFERENCE BY $4{\cdot}0 \times 10^{-4}M$ TANTALUM IN THE DETERMINATION OF $2{\cdot}0 \times 10^{-5}M$ NIOBIUM.

Pyrogallol, *g*/50 *ml*	Relative error, %	
	Direct	Corrected
0·4	−62·5	
0·8	−39·1	
2·0	+30·4	
3·0	+23·7[a]	−5·2
4·0	+44·5[a]	+15·6
5·0	+155·5[b]	

[a] Measured against a blank of 0·4 g of pyrogallol per 50 ml; no visible colour from oxidation of pyrogallol but some absorbance may have been present from that source.
[b] Noticeable off-colour from pyrogallol oxidation.

sample containing only tantalum, this element was shown to extract 87% quite consistently (in the presence of both pyrogallol and Ethoquad) up to an initial aqueous concentration of $5{\cdot}0 \times 10^{-4}M$, at which point the absorbance of the extract levelled off while that of the aqueous phase continued to increase. Therefore, the low niobium results must be caused by depletion of pyrogallol by the tantalum. The trend in absorbance with added pyrogallol (Table IV) tends to confirm this explanation although coloured oxidation products obviously contributed to the positive error at the highest concentration of pyrogallol.

The present procedure should yield satisfactory results for niobium samples when

the niobium-tantalum ratio is unity or greater. Best results would be obtained by working with a dilute sample to minimise the tantalum interference. If an independent determination of tantalum were made, the accuracy of some results for smaller ratios should be improved by applying the correction for the absorbance of tantalum.

If boric acid is added to the sample before extraction, approximately 95% of the tantalum remains in the aqueous phase. This indicates that tantalum is extracted in the form of a fluoride complex, probably TaF_7^{2-}. It also suggests a promising approach for a future study of the separation of tantalum and niobium.

Fluoride and phosphate. Concentrations of species as high as $4{\cdot}0 \times 10^{-2}M$, representing anion-to-niobium ratios of up to 2000, introduced insignificant (<2%) errors into the direct and the extraction procedures.

DISCUSSION

In the presence of a long-chain quaternary ammonium ion, the niobium-pyrogallol complex reacts to give a more highly absorbing species than otherwise and, in addition, the resulting species is extractable. The nature of the species is largely unknown although brief studies of combining ratios have indicated that 2:5 and 1:5 niobium: ammonium combinations exist.

A rapid qualitative test using the ammonium form of Dowex 50 W × 8 and the oxalate form of Dowex 3 showed little exchange of the niobium and tantalum pyrogallol-Ethoquad complexes by the former, but extensive exchange by the latter. In contrast, vanadium and chromium disappeared completely on to the cation exchanger but were unaffected (except for slow reduction of vanadium on the beads) by the anion exchanger. It appears, therefore, that interference from vanadium might be virtually eliminated by prior contact with a cation exchanger.

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Zusammenfassung—Die optische Absorption einer Mischung von Niob(V) und Pyrogallol in leicht alkalischem Medium wird um etwa 60% erhöht, wenn eine langkettige quaternäre Ammonium-Verbindungen zugesetzt wird. Zusätzlich wird die Störung durch Mo(VI), W(VI) und Cr(VI) praktisch vollkommen ausgeschaltet und die von V(V) auf die Hälfte reduziert, wenn der Niobkomplex mit Äthylacetat ausgezogen wird. Tantal wird mit ausgezogen, seine Störung kann jedoch durch geeignete Wahl der Wellenlänge wesentlich vermindert werden. Die Störung durch Ti ist erheblich, jedoch etwas geringer als in der Original Methode von Hunt und Wells.

Résumé—L'absorption optique produite par le mélange niobium(5)-pyrogallol en solution faiblement alcaline est augmentée d'environ 60% par la présence d'un sel d'ammonium quaternaire à longue chaîne. De plus, les interférences du molybdène(VI), du tungstène(VI) et du chrome(VI) peuvent être pratiquement éliminées et celle du vanadium (V) réduite de moitié en extrayant le complexe du niobium par l'acétate d'éthyle. Le tantale accompagne le niobium, mais, en choisissant convenablement la longueur d'onde, on peut diminuer l'interférence due à de faibles quantités. L'interférence du titane est trés sérieuse, mais un peu moins que dans la méthode originale de Hunt et Wells.

REFERENCES

[1] R. I. Alekseev, *Zavodskaya Lab.*, 1938, **7**, 863; *Chem. Abs.*, 1939, **33**, 498.
[2] I. P. Alimarin and R. L. Podval'naya, *Zhur. analyt. Khim.*, 1946, **1**, 30; *Chem. Abs.*, 1949, **43**, 2543d.
[3] M. N. Bukhsh and D. N. Hume, *Analyt. Chem.*, 1955, **27**, 116.
[4] G. Charlot and J. Saulnier, *Chim. analyt.*, 1953, **35**, 51.
[5] A. Eder, *Arch. Eisenhüttenw.*, 1955, **26**, 431; *Chem. Abs.*, 1955, **49**, 13830e.
[6] I. Geld and J. Carroll, *Analyt. Chem.*, 1949, **21**, 1098.
[7] H. Goto and Y. Kakita, *Science Reports Res. Inst. Tôhoku Univ., Ser. A*, 1950, **2**, 249; *Chem. Abs.*, 1951, **45**, 7913i.

[8] J. L. Hague and L. A. Machlan, *J. Res. Nat. Bur. Stand.*, 1959, **62,** 11.
[9] R. D. Hall and E. F. Smith, *Proc. Amer. Phil. Soc.*, 1905, **44,** 196.
[10] *Idem, J. Amer. Chem. Soc.*, 1913, **35,** 138.
[11] J. Hastings and T. A. McClarity, *Analyt. Chem.*, 1954, **26,** 683.
[12] E. C. Hunt and R. A. Wells, *Analyst*, 1954, **79,** 345.
[13] L. Ikenberry, J. L. Martin and W. J. Boyer, *Analyt. Chem.*, 1953, **25,** 1340.
[14] P. Klinger and W. Koch, *Arch. Eisenhüttenw.*, 1939, **13,** 127; *Chem. Abs.*, 1939, **33,** 9186.
[15] A. B. H. Lauw-Zecha, S. S. Lord, Jr. and D. N. Hume, *Analyt. Chem.*, 1952, **24,** 1169.
[16] K. S. Lee, E. O. Price and J. E. Land, *J. Amer. Chem. Soc.*, 1956, **78,** 1325.
[17] W. J. Maeck, G. L. Booman, M. E. Kussy and J. E. Rein, 140th ACS Natl. Meeting, Anal. Div., Chicago, Sept. 3–8, 1961.
[18] C. Matignon, *Compt. rend.*, 1904, **138,** 82.
[19] J. P. McKaveney, *Analyt. Chem.*, 1961, **33,** 744.
[20] M. G. Mellon, Symposium on Structure and Properties of Heteropolyanions, ACS, Div. of Phys. and Inorg. Chem., Atlantic City, Sept. 17, 1956.
[21] J. Moir, *J. Chem., Met., Mining, Soc. S. Africa*, 1916, **16,** 191; *Chem. Abs.*, 1916, **10,** 1825.
[22] F. C. Palilla, N. Adler and C. F. Hiskey, *Analyt. Chem.*, 1953, **25,** 926.
[23] M. S. Platonov and N. F. Krivoshlykov, *Trudy Vsesoytuz. Konferentsii Anal. Khim.*, 1943, **2,** 359; *Analyst*, 1948, **73,** 175; *Chem. Abs.*, 1945, **39,** 3492.
[24] M. S. Platonov, N. F. Krivoshlykov and A. A. Marakaev, *J. Gen. Chem. (U.S.S.R.)*, 1936, **6,** 1815; *Chem. Abs.*, 1937, **31,** 4614.
[25] E. Plsko, *Chem. Zvesti*, 1958, **12,** 95; *Chem. Abs.*, 1960, **52,** 11642f.
[26] E. Pozzi-Escot, *Compt. rend.*, 1904, **138,** 200.
[27] A. Rosenheim and O. Sorge, *Ber.*, 1920, **53,** 932.
[28] S. Ya. Shnaiderman, *Ukrain. khim. Zhur.*, 1957, **23,** 92; *Chem. Abs.*, 1957, **51,** 10307c.
[29] G. Telep and D. F. Boltz, *Analyt. Chem.*, 1952, **24,** 163.
[30] G. Thanheiser, *Mitt. Kaiser Wilhelm-Inst. Eisenforsch., Dusseldorf*, 1940, **22,** 255; *Chem. Abs.*, 1941, **35,** 2438.
[31] F. N. Ward and A. P. Marranzino, *Science*, 1954, **119,** 655; *Analyt. Chem.*, 1955, **27,** 1325.
[32] D. F. Wood and I. R. Scholes, *Analyt. Chim. Acta*, 1959, **21,** 121.
[33] M. Yana, H. Mochizuki, R. Hayiyama and T. Misaki, *Japan Analyst*, 1955, **4,** 499; *Chem. Abs.*, 1956, **50,** 16548d.

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IMPROVED DETERMINATION OF TANTALUM BASED UPON THE PYROGALLOL PROCEDURE

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Summary—The pyrogallol method for tantalum has been improved in two ways. First, the addition of boric acid eliminates the interference from fluoride. Second, incorporation of an extraction with ethyl acetate, in the presence of a long-chain quaternary ammonium ion, eliminates the interference from vanadium^{V} and decreases that from chromium^{VI}. Titanium^{VI}, molybdenum^{VI} and tungsten^{VI} remain as interferences.

INTRODUCTION

FOR a study involving the enrichment of tantalum by foam fractionation, the pyrogallol method[2–9,13,15] was preferred because of its known compatibility with the foam-producing quaternary ammonium surfactant. The adopted analytical procedure closely follows that of Hunt and Wells[6] with two exceptions. First, Ethoquad, a quaternary ammonium chloride, is added to make possible the extraction of vanadium and chromium, and thereby greatly reduce interference from these ions. Second, because hydrofluoric acid is frequently used to dissolve samples, boric acid was also added to complex free fluoride ion. The usual Hunt and Wells procedure involves fusion of a sample with bisulphate, followed by dissolution of the melt in a solution of ammonium oxalate and development of a colour with pyrogallol. The tantalum procedure is closely related to the one for niobium, the chief difference being the acidic medium used for tantalum as opposed to a weakly alkaline one for niobium.

EXPERIMENTAL

Reagents

In general, the reagents were the same as those for the determination of niobium.[1] Finely powdered ammonium oxalate (Mallinckrodt) and boric acid (Merck) were used.

Pyrogallol reagent:[6] A 5-ml portion of 1 : 1 sulphuric acid was added to 20 g of pyrogallol followed by 70 ml of water. After dissolution of the crystals, the solution was filtered and diluted to 100 ml with water. After 5 days, the reagent was unchanged or, at the most, slightly pink.

Wash solution: A mixture of 20 ml of 0·5*M* sodium fluoride, 80 ml of $1{\cdot}0 \times 10^{-3}M$ Ethoquad 18/25 (polyethoxy [15] stearylmethylammonium chloride from Armour and Co.), 40 ml of 9% sodium bisulphate and 20 ml of 1*M* sodium hydroxide solution was diluted to 200 ml with distilled water. The final pH was slightly above 3·0.

Procedure

Add to an appropriate aliquot of the sample solution, as prepared by the Hunt and Wells procedure,[6] 1 g of boric acid, 20 ml of aqueous $1{\cdot}0 \times 10^{-3}M$ Ethoquad and 4 ml of pyrogallol reagent. Dilute with water to 50 ml and shake until a clear solution remains before reading the optical absorbance at 400 mμ.

When vanadate and/or chromate is present, the final solution should be extracted before measuring the absorbance. Treat 25 ml of solution successively with 10-, 5- and 5-ml portions of ethyl acetate. (These extracts after being shaken with three 5-ml portions of wash solution, then filtered through anhydrous sodium sulphate, may be used to determine vanadium or chromium by measuring the

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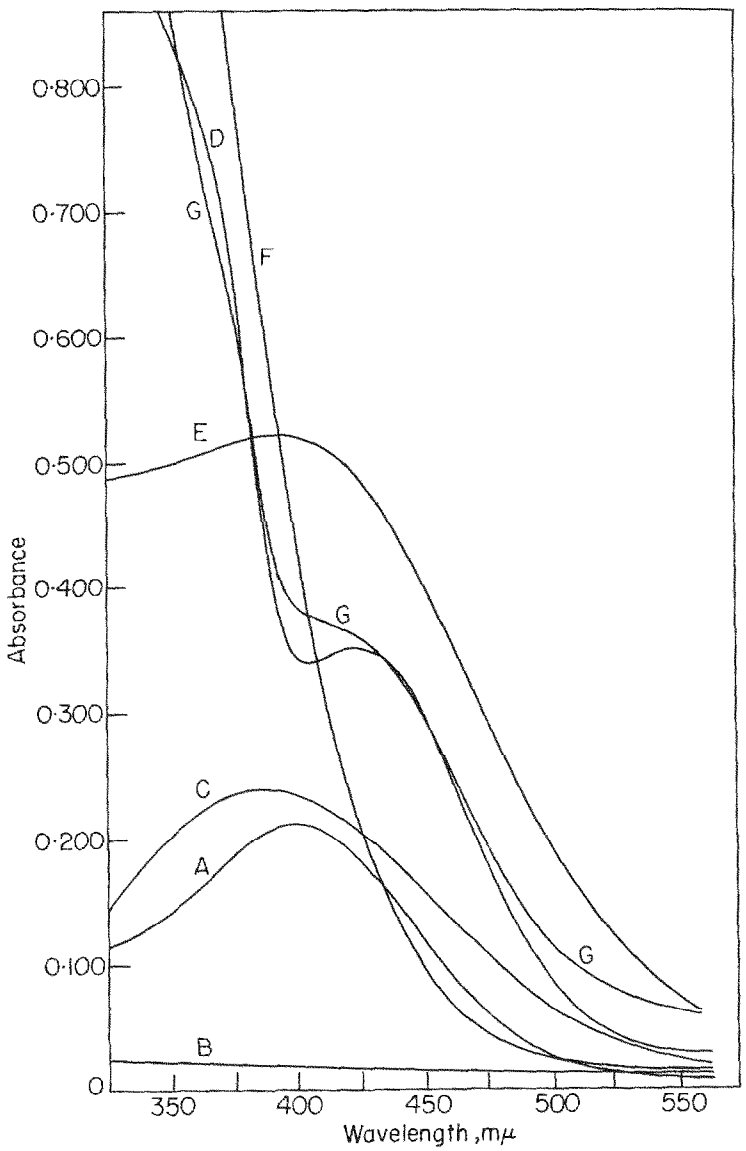


FIG. 1.—Spectra for tantalum and certain interfering ions in the aqueous solution before extraction:

A—$1{\cdot}0 \times 10^{-4}M$ Ta,
B—$2{\cdot}0 \times 10^{-4}M$ Nb,
C—$1{\cdot}0 \times 10^{-4}M$ Ti,
D—$1{\cdot}0 \times 10^{-3}M$ V,
E—$5{\cdot}0 \times 10^{-4}M$ Mo,
F—$1{\cdot}0 \times 10^{-3}M$ W,
G—$5{\cdot}0 \times 10^{-4}M$ Cr,

absorbance at 420 mμ.) Tantalum remains in the original aqueous phase which is filtered through wet filter paper. The absorbance is measured on the last filtered portion, and it is linear up to $3 \times 10^{-4}M$ tantalum, the highest concentration tested, for which the absorbance was 0·645.

RESULTS

Preliminary studies

An attempt to substitute ammonium citrate for ammonium oxalate led to a large decrease in the absorbance. Even though the residual absorbance values were linear with the tantalum concentration, the sensitivity was so poor that the use of citrate was abandoned. Parenthetically, it is of interest to note that citrate enhanced the intensity of the vanadium colour without affecting its extractability into ethyl acetate.

Although earlier investigators warned of interference from excess fluoride, provisions for its elimination are seldom mentioned.[5] A few experiments confirmed that the presence of excess boric acid eliminated the fluoride interference, increased the absorbance, and produced a linear relationship with the tantalum concentration. By comparing the absorbance values for two portions of a tantalum sample, one of which has not been treated with boric acid, one should be able to measure the fluoride present.

The presence of Ethoquad was found to exert no effect upon the absorbance or the extraction behaviour of tantalum. It was retained as a reagent because it makes possible the elimination of interference from chromium and vanadium.

The pH of 3·0 to 3·2 recommended by Hunt and Wells[6] has been retained. However, it was observed that an absorbance value nearly 25% greater was obtained at pH 3·5. This emphasised the need to control carefully the final pH.

TABLE I.—INTERFERENCES, IN TERMS OF TANTALUM, FROM 1 MILLIMOLE OR 1 MG OF CERTAIN METAL IONS[a]

Ion	Concn. units	Hunt and Wells[6]	$4{\cdot}0 \times 10^{-4}M$ Ethoquad added		
			Direct	Extracted	Extracted; H_3BO_3 present
Mo^{VI}	mmoles	0·27	0·49	—	—
	mg	0·51	0·92	—	—
W^{VI}	mmoles	0·11	0·20	—	—
	mg	0·11	0·20	—	—
V^{V}	mmoles	0·26	0·16	0·035	0·00
	mg	0·92	0·57	0·125	0·00
Cr^{VI}	mmoles	not mentioned	0·36	0·093	0·093
	mg	not mentioned	1·25	0·32	0·32
Ti^{IV}	mmoles	0·99	1·09	—	—
	mg	3·74	4·12	—	—
Nb^{V}	mmoles	0·0051	0·044	0·038	—
	mg	0·0100	0·086	0·074	—

[a] Calculated for $1{\cdot}0 \times 10^{-4}M$ tantalum from the absorption of the pure interference.

Interferences

Molybdenum^{VI}. The yellow-to-orange colour is a molybdenum-pyrogallol complex for which a 2:3 ratio[12] and a 1:1 ratio at pH 3·5[10] have been reported. Unfortunately, the colour is not extracted by ethyl acetate so that its interference is serious

(see Table I). Phosphate and fluoride, up to $4{\cdot}0 \times 10^{-2}M$ do not affect the intensity of the colour.

Tungsten^{VI}. The 1:1 tungsten-pyragallol complex at pH 3·5[10] has a greenish-yellow colour. It interferes seriously because it is not extractible. The intensity of the colour is gravely affected by fluoride; it could be increased by the presence of boric acid or completely destroyed by added fluoride. The colour could be largely destroyed by adding phosphate.

Vanadium^{V}. On adding pyrogallol, a transient violet colour appears before the solution turns yellow-orange. The vanadium-pyrogallol colour is reported[12] to have a ratio of 2:3. The intensity is decreased by boric acid, but as shown in Table I, boric acid increases the extractibility of vanadium from about 85% to 100%, thereby entirely eliminating its interference. In fact, the absorbance values for extracts ob-

TABLE II.—EFFECT OF NIOBIUM ON THE DETERMINATION OF $1{\cdot}2 \times 10^{-4}M$ TANTALUM

Molar ratio of Nb:Ta	Absorbance	Error, %
—	0·273	—
1:10	0·271	−0·73
1:5	0·271	−0·73
1:1	0·271	−0·73
2:1	0·266	−2·56
4:1	0·253	−7·33
8:1	0·237	−13·2
16·7:1	0·228	−16·5

tained using the recommended procedure have been checked and found to agree, within experimental error, with the aqueous extracts before extraction. Furthermore, the relationship between absorbance and concentration was linear up to $1{\cdot}0 \times 10^{-3}M$ (an absorbance of 0·245).

The intensity for vanadium in the aqueous phase is not affected by fluoride. In the presence of $4{\cdot}0 \times 10^{-2}M$ phosphate, partial reduction of vanadium occurs.

Chromium^{VI}. The yellow colour developed by chromium is greenish in dilute solution and brownish in concentrated solution. It is unaffected by fluoride and phosphate (up to $4{\cdot}0 \times 10^{-2}M$). Although the chromium colour appears to be extractible into ethyl acetate, some colour which is probably an oxidation product of pyrogallol, remains in the aqueous phase to interfere with the tantalum determination. Boric acid had no effect on the interference.

Titanium^{IV}. The yellow colour of titanium is even more sensitive than that of tantalum. A titanium-pyrogallol ratio of 1:4 has been reported to exist in weakly acidic media.[11] The colour is not extractible and hence other separation procedures such as ion exchange[5,14] must be applied.

Niobium^{V}. For unexplained reasons, the interference from niobium was found to be nearly ten times as large as that reported by Hunt and Wells.[6] Table I shows that some niobium is removed by extraction.

Table II is a representative set of data that shows the negligible interference of niobium up to a level equivalent to tantalum. At higher levels of niobium, the errors for tantalum were negative in spite of adding additional pyrogallol to counteract that lost by reaction with niobium.

DISCUSSION

This new procedure for tantalum incorporates boric acid and thereby eliminates the interference from fluoride. In fact, it has been found that the fluoride in a solution of tantalum can be determined by measuring the absorbances in the absence and in the presence of boric acid.

Another advantage of the proposed procedure is the elimination of interference from vanadium. Although the presence of citrate greatly diminishes the absorbance of tantalum, it increases that for vanadium. Hence, the use of citrate may prove to be advantageous for determining vanadium in the presence of tantalum.

Titanium and, to a lesser extent, molybdenum and chromium interfere seriously. An earlier paper[1] has pointed out the possibility of removing chromium by cation exchange. Examination of the ion-exchange behaviour of titanium and molybdenum appears to be desirable because of the possibility that they might easily be removed in this way.

The interference data in Table I were calculated on the basis of absorbance measurements for the interfering element in the absence of tantalum. Although tests of binary mixtures yielded results which generally agreed with Table I, it is important to note that niobium, instead of giving a small positive interference, actually gave a negative interference because of depletion of pyrogallol (Table II).

Another possibility which would eliminate any interference from chromium and molybdenum, would be to extract the tantalum under conditions used for niobium. Back extraction of tantalum (and much of the niobium) into an acidic aqueous medium should remove all of the interferences listed in Table I except titanium. Unfortunately, time did not permit this modification to be tested.

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Zusammenfassung—Die Pyrogallolmethode für Tantal wurde in doppelter Hinsicht verbessert. Ersten wird die Störung durch Borsäure mittels Zugabe von Fluorid ausgeschaltet. Zweitens wurde eine Extraktion mit Äthylacetat eingeschaltet, und zwar in Gegenwart einer langkettigen quaternären Ammoniumbase, wodurch die Störung durch V(V) ausgeschaltet und die durch Cr(VI) vermindert wird. Ti(IV), Mo(VI) und W(VI) stören nach wie vor.

Résumé—La méthode au pyrogallol pour le dosage du tantale a été améliorée de deux manières. D'abord, l'addition d'acide borique élimine l'interférence du fluorure. D'autre part, une extraction par l'acétate d'éthyle, en présence d'un ion ammonium quaternaire à longue chaîne, élimine l'interférence du vanadium(V) et diminue celle du chrome(VI). Il reste encore les interférence du titane(IV) du molybdène (VI) et du tungstène(VI).

REFERENCES

[1] J. A. Catoggio and L. B. Rogers, *Talanta*, 1962, **9**, 377.
[2] J. I. Dinnin, *Analyt. Chem.*, 1953, **25**, 1803.
[3] A. Eder, *Arch. Eisenhuttenw.*, 1955, **26**, 431; *Chem. Abs.*, 1955, 49, 13830e.
[4] H. Goto and Y. Kakita, *Science Reports Res. Inst. Tôhoku Univ., Ser. A*, 1950, **2**, 249; *Chem. Abs.*, 1951, **45**, 7913i.
[5] J. L. Hague and L. A. Machlan, *J. Res. Nat. Bur. Stand.*, 1959, **62**, 11.
[6] E. C. Hunt and R. A. Wells, *Analyst*, 1954, **79**, 345.
[7] L. Ikenberry, J. L. Martin and W. J. Boyer, *Analyt. Chem.*, 1953, **25**, 1340.
[8] G. Norwitz, M. Codell and J. J. Mikula, *Analyt. Chim. Acta*, 1954, **11**, 173.
[9] M. S. Platanov and N. F. Krivoshlykov, *Trudy Vsesoyuz. Konferentsii Anal. Khim.*, 1943, **2**, 359; *Analyst*, 1948, **73**, 175; *Chem. Abs.*, 1945, **39**, 3492[4].

[10] E. Plško, *Chem. Zvesti*, 1958, **12**, 95; *Chem. Abs.*, 1960, **52**, 11642f.
[11] S. Ya Shnaĭderman, *Ukrain. khim. Zhur.*, 1957, **23**, 92; *Chem. Abs.*, 1957, **51**, 10307c.
[12] S. Ya. Shnaĭderman and G. I. Khrustalev, *Zhur. obshchei Khim.*, 1959, **29**, 20; *Chem. Abs.*, 1959, **53**, 17756c.
[13] G. Thanheiser, *Mitt. Kaiser Wilhelm-Inst. Eisenforsch, Dusseldorf*, 1940, **22**, 255; *Chem. Abs.*, 1941, **35**, 2438[8].
[14] D. H. Wilkins, *Talanta*, 1959, **2**, 355.
[15] M. Yana, H. Mochizuki, R. Kajiyama and T. Misaki, *Japan Analyst*, 1955, **4**, 499; *Chem. Abs.*, 1956, **50**, 16548d.

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ION-EXCHANGE SEPARATIONS USING SULPHOSALICYLIC ACID*

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Summary—Ion-exchange separation of metal cations is carried out by elution from a 4- to 8-cm cation-exchange column with sulphosalicylate at pH 6 to 7. Aluminium^{III}, iron^{III}, titanium^{IV}, uranium^{VI}, vanadium^{IV} and zirconium^{IV} are quantitatively eluted, and thorium^{IV} and copper^{II} are partly eluted. Other bivalent metal ions and rare earths are quantitatively retained by the column.

A FEW investigators have used sulphosalicylic acid as a complexing agent for ion-exchange separation of metal cations. Schubert *et al.*[1] separated beryllium^{II} from copper^{II} and from uranium^{VI} using a cation-exchange column. Beryllium^{II} is eluted with sulphosalicylate at pH 3·5. Copper^{II} remains on the column and is stripped off with 3*M* sulphuric acid. In the beryllium–uranium separation, beryllium^{II} is eluted with sulphosalicylic acid adjusted to pH 4·6 to 4·7. Alimarin and Tsintsevich[2] separated gallium^{III} from zinc^{II} by elution of gallium from a cation-exchange column with pH 10 sulphosalicylate. Oliver and Fritz[3] separated several binary mixtures with fair success using either cation- or anion-exchange columns with sulphosalicylate eluent at pH 8 to 10.

A number of useful and quantitative ion-exchange separations not previously reported can be accomplished. Our separations are carried out on a very short (4- to 8-cm) cation-exchange column by elution with sulphosalicylate at pH 6 to 7. Following separation, the metal ions are determined by titration with EDTA or by other standard analytical methods.

EXPERIMENTAL

Reagents

Ion exchange resin: "Analyzed reagent" Dowex 50W X8, 100–200 mesh, sodium-form resin was used. The resin was regenerated by elution of a large batch with 3*M* hydrochloric acid, followed by an aqueous rinse and elution with 10% diammonium hydrogen citrate adjusted to pH 3·0 to 3·5 with hydrochloric acid. After another aqueous rinse, the resin was converted to the sodium form by elution with 10% sodium chloride. The resin was washed with water until a negative chloride test was obtained.

Ion-exchange paper: Reeve Angel type SA-2 ion-exchange loaded paper was used. This contains about 55% Amberlite IR-120 resin in the sodium form.

EDTA [*disodium dihydrogen(ethylenedinitrilo)tetra-acetate dihydrate*]: A 0·05*M* solution was prepared from Eastman white label material and standardised by titration of a zinc solution prepared from very pure zinc metal.

Sulphosalicylic acid: A 0·15*M* aqueous solution was used.

Acetic buffer: The solution used was 0·05*M* in sodium acetate and 0·0026*M* in sulphosalicylate. Before use, the pH was adjusted to the desired value with solium hydroxide or perchloric acid. A 0·10*M* acetate buffer was similarly prepared, but contained twice the amount of sodium acetate.

All other solutions were prepared from Reagent Grade chemicals.

* Contribution No. 1088. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

Ion-exchange paper chromatography

Strips of ion-exchange paper, 3·5 × 30·5 cm, were placed in the troughs of a chromatography cabinet. A buffer solution, 0·2*M* in ammonium acetate and 0·008*M* in sulphosalicylate, of appropriate pH, was placed in the troughs and allowed to percolate down the ion-exchange paper overnight. The papers were rinsed with water. Metal sulphosalicylate solutions were prepared by mixing 2 ml of 0·05*M* metal ion solution, 6 ml of 0·2*M* buffer and 3 ml of 0·15*M* sulphosalicylic acid. The pH was adjusted with dilute ammonia or perchloric acid. Using a 200-microlitre pipette, the samples were applied to the paper 23 cm from the bottom of the paper. The papers were eluted with 0·2*M* buffer. A dry paper was also placed in the trough to ascertain the distance travelled by the eluent. The papers were air dried, and the location of the metal ions was determined by appropriate qualitative tests.

Ion-exchange column separations

Add a slurry of Dowex 50W X8, 100–200 mesh, sodium-form resin to a 2·2 × 8-cm ion-exchange column until a resin bed approximately 4 cm high is obtained. Buffer the resin by adding 75 to 140 ml of 0·05*M* acetate buffer at a rate of 8 to 13 ml per min. The pH of the last effluent should be within 0·05 pH unit of the desired value.

To a sample mixture containing 0·05 to 0·5 mmole of each metal ion, add an amount of 0·15*M* sulphosalicylic acid equivalent to three times the molar concentration of total metal ion. Add 30 ml of acetate buffer and adjust the pH to the required value with sodium hydroxide or perchloric acid. (If titanium^{IV} is present, adjust the pH with dilute ammonia). Add the sample thus prepared to the column at a flow rate of 8 to 13 ml per min. Rinse the sample through the column with three 30-ml rinses of acetate buffer solution.

After the sulphosalicylate elution, strip the element(s) remaining on the column with strong acid. Most elements are eluted with 150 ml of 3*M* hydrochloric acid; rare earths and yttrium require 350 to 450 ml of 4*M* hydrochloric acid. Elute lead^{II} with 150 ml of 4*M* nitric acid.

Determination of metal ions

Effluents containing Al, Th, Ti, U and V must be treated with nitric and perchloric acids to destroy the sulphosalicylic acid before analysis. Evaporate the effluent to about 30 ml. Add 10 ml of concentrated nitric acid and evaporate to about 15 ml. Add 10 ml more of nitric acid and 10 ml of 70–72% perchloric acid, and evaporate to fumes of perchloric acid. Add an additional 10 ml of perchloric acid and evaporate nearly to dryness. (If Ti is present add 2 ml of concentrated sulphuric acid). Evaporate effluents containing metal ions eluted with hydrochloric or nitric acid nearly to dryness to remove excess acid before titration.

TABLE 1.—R_f VALUES FOR METAL IONS ON CATION-EXCHANGE PAPER USING SULPHOSALICYLATE ELUENT

Metal ion	pH	Range of R_f values	Average R_f
Fe^{III}	5·0	0–0·41	0·20
	6·0	0·13–0·45	0·29
U^{VI}	5·0	0–0·28	0·14
	6·0	0–0·31	0·16
Ti^{IV}	5·0		>0
	6·0		>0
Zr^{IV}	5·0		>0
	6·0		>0
Co^{II}	6·0	0	0
La^{III}	7·0	0	0
Th^{IV}	6·0	0–0·44	0·22
Y^{III}	6·0	0	0
	7·0	0	0
Cu^{II}	5·0	0·03–0·09	0·06
	6·0	0·07–0·25	0·16
Hg^{II}	6·0	0	0
	7·0	0	0
Zn^{II}	7·0	0	0
Ni^{II}	6·0	0	0
	7·0	0	0

The methods of determination used are summarised below.

EDTA: Standardise by titrating standard zinc^{II} solution using naphthyl azoxine[4] and Eriochrome Black T[5] as indicators.

Lanthanum^{III}, *yttrium*^{III}, *ytterbium*^{III}: EDTA titration using arsenazo indicator.[6]

Copper^{II}, *cadmium*^{II}, *zinc*^{II}, *cobalt*^{II}, *lead*^{II}, *nickel*^{II}: EDTA titration using naphthyl azoxine indicator.[7]

Aluminium^{III}: Addition of excess EDTA and back-titration with zinc^{II} in 50% ethyl alcohol using dithizone indicator.[8]

Thorium^{IV}: EDTA titration using Xylenol Orange indicator.[5]

Titanium^{IV}: Addition of hydrogen peroxide and excess EDTA, and back-titration with copper^{II} using naphthyl azoxine indicator.[9]

Mercury^{II}: Titration at pH 6 with 1-mercapto-2,3-diol solution using thio-Michler's ketone indicator.

Manganese^{II}: EDTA titration in the presence of ascorbic acid and potassium cyanide, Eriochrome Black T indicator.[10]

Magnesium^{II}: EDTA titration in the presence of ascorbic acid, triethanolamine and potassium cyanide, Eriochrome Black T indicator.[10]

Uranium^{VI}: Determination by the oxidation-reduction method of Sill and Peterson.[11]

Iron^{III}: Photometric titration with EDTA at 500 mμ.[12]

Zirconium^{IV}: Gravimetric determination using mandelic acid as precipitating reagent.[13]

Vanadium^{IV}: EDTA titration.[9]

RESULTS

Ion-exchange paper chromatography was used to explore the scope of sulphosalicylate elutions and to predict suitable conditions for ion-exchange column separations. The R_f values given in Table I indicated that the elution of iron^{III}, titanium^{IV}, uranium^{VI} and zirconium^{IV} is feasible at pH 5 to 7. R_f values for bivalent metal ions except copper^{II} were zero, indicating that these are not eluted.

Elution of several individual metal ions from an ion-exchange column showed that iron^{III}, aluminium^{III}, titanium^{IV} and vanadium^{IV} are quantitatively eluted at pH 6·0. Thorium^{IV} and copper^{II} are incompletely eluted. Cobalt^{II} and other bivalent metal ions are quantitatively retained by the ion-exchange column.

When quantitative separation of mixtures was attempted it was found that iron^{III}, aluminium^{III}, titanium^{IV}, uranium^{VI}, vanadium^{IV} and zirconium^{IV} are quantitatively eluted and that cobalt^{II}, cadmium^{II}, lanthanum^{III}, lead^{II}, magnesium^{II}, nickel^{II}, ytterbium^{III}, yttrium^{III} and zinc^{II} are quantitatively retained on the column. Results for typical quantitative separations are given in Table II. Although most separations were carried out on approximately equimolar binary mixtures, several successful separations were performed where the mole-ratio of eluted to retained ion was either 10:1 or 1:10.

The separation of uranium and lead failed because of the formation of a precipitate. An attempted separation of aluminium and manganese originally resulted in the elution of part of the manganese^{II} with the aluminium^{III}. However, the addition of ascorbic acid prevented any oxidation of manganese^{II} to a manganese^{III} complex, and permitted a quantitative separation of aluminium and manganese. Thorium is incompletely eluted, apparently because of the unusually high affinity of the cation-exchange resin for thorium^{IV}. The separation of aluminium^{III} and yttrium^{III} at a 1:10 mole ratio is successful only if the amount of buffer is twice the usual quantity.

Although individual results are reported in Table II, most separations were actually done in duplicate or triplicate. The average recovery for all separations was 100·5% with an average deviation of $\pm$0·4%. The bias toward high results probably represents a pick-up of impurities from the reagents used in separation.

TABLE II.—ION-EXCHANGE COLUMN SEPARATIONS

Metal ion pairs	pH	Taken, *mg*	Found, *mg*	Difference, *mg*
Al^{III}	6·0	6·59	6·60	+0·01
Zn^{II}	6·0	16·44	16·44	0·00
Al^{III}	6·1	13·22	13·23	+0·01
Zn^{II}	6·1	3·20	3·26	+0·06
Al^{III}	6·1	6·59	6·63	+0·04
Mn^{II}	6·1	14·27	14·51	+0·24
Al^{III}	6·0	6·58	6·59	+0·01
Mg^{II}	6·0	5·44	5·47	+0·03
Al^{III}	6·0	1·38	1·38	0·00
Mg^{II}	6·0	10·84	10·86	+0·02
Al^{III}	6·0	1·38	1·39	+0·01
Ni^{II}	6·0	29·08	29·11	+0·03
Al^{III}	6·0	6·59	6·62	+0·03
Pb^{II}	6·0	49·43	48·10	−1·33
Al^{III}	6·1	6·59	6·65	+0·06
La^{II}	6·1	28·47	28·47	0·00
Al^{III}	6·0	13·20	13·18	−0·02
Y^{II}	6·0	5·05	5·05	0·00
Al^{III}	6·2	1·38	1·37	−0·01
Y^{II}	6·2	51·24	51·19	−0·05
Fe^{III}	6·1	14·47	14·68	+0·21
Co^{II}	6·1	14·70	14·67	−0·03
Fe^{III}	6·1	14·45	14·48	+0·03
Ni^{II}	6·1	14·44	14·35	−0·09
Fe^{III}	6·1	14·45	14·45	0·00
Zn^{II}	6·1	16·44	16·50	+0·06
Fe^{III}	6·1	14·45	14·48	+0·03
Mg^{II}	6·1	5·44	5·47	+0·03
Fe^{III}	6·1	14·51	14·54	+0·03
Cd^{II}	6·1	27·76	27·93	+0·17
Fe^{III}	6·2	14·48	14·51	+0·03
La^{III}	6·2	28·47	28·47	0·00
Fe^{III}	6·2	14·48	14·54	+0·06
Pb^{II}	6·2	49·43	49·53	+0·10
Fe^{III}	6·3	14·54	14·54	0·00
Y^{III}	6·3	25·47	25·47	0·00
Fe^{III}	6·3	14·59	14·54	−0·05
Yb^{II}	6·3	46·15	46·15	0·00
Ti^{IV}	6·0	11·11	11·28	+0·17
Co^{II}	6·0	14·70	14·73	+0·03
Ti^{IV}	6·0	11·11	11·25	+0·14
Ni^{II}	6·0	14·46	14·46	0·00
Ti^{IV}	6·0	11·11	11·20	+0·09
Mg^{II}	6·0	5·42	5·48	+0·06
U^{VI}	6·2	60·18	60·05	−0·13
Cu^{II}	6·2	16·26	16·38	+0·12
U^{VI}	6·1	60·12	59·79	−0·33
Ni^{II}	6·1	14·46	14·52	+0·06
U^{VI}	6·7	60·52	60·59	+0·07
Cd^{II}	6·7	27·82	27·98	+0·16
U^{VI}	6·1	60·52	60·37	−0·15
La^{III}	6·1	28·47	—	—
U^{VI}	6·7	60·89	60·74	−0·15
Mg^{II}	6·7	5·42	5·42	0·00
U^{VI}	6·9	121·5	121·6	+0·1
Co^{II}	6·9	29·46	29·46	0·00

TABLE II.—*(continued.)*

Metal ion pairs	pH	Taken, *mg*	Found, *mg*	Difference, *mg*
V^{IV}	6·1	20·20	20·22	+0·02
Co^{II}	6·1	29·49	29·49	0·00
V^{IV}	6·1	10·10	10·20	+0·10
Mg^{II}	6·1	5·42	5·33	+0·11
V^{IV}	6·0	2·42	2·48	+0·06
Zn^{II}	6·0	32·77	32·87	+0·10
Zr^{IV}	6·0	27·25	—	—
Co^{II}	6·0	14·78	14·78	0·00
Zr^{IV}	6·1	27·25	27·10	−0·15
Zn^{II}	6·1	16·40	16·43	+0·03

Zusammenfassung—Ionenaustauschertrennung von Metallionen wird erzielt, indem von 4–8 cm Säulen mit Sulfosalizylsäure bei pH 6–7 eluiert wird. Al, Fe(III), Ti(IV), U(VI), V(IV) and Zr werden quantitativ eluiert; Th und Cu(II) nur teilweise. Zweiwertige Metallionen und seltene Erden verbleiben quantitativ in der Säule.

Résumé—La séparation par échange d'ions de cations métalliques est réalisée par élution sur une colonne de 4 à 8 cm avec le sulfosalicylate à pH 6 à 7. L'aluminium(III), le fer(III), le titane(III) élués quantitativement; le thorium(IV) et le cuivre(II) ne sont élues qu'en partie. Les autres ions métalliques divalents et les terres rares sont retenus quantitativement par la colonne.

REFERENCES

[1] J. Schubert, A. Lindenbaum and W. Westfall, *J. Phys. Chem.*, 1958, **62**, 390.
[2] I. P. Alimarin and E. P. Tsintsevich, *Zavodskaya Lab.*, 1956, **22**, 1276.
[3] R. T. Oliver and J. S. Fritz, *U.S. Atomic Comm. Report* ISC-1056, June 1958.
[4] L. Granatelli, *Analyt. Chem.*, 1959, **31**, 434.
[5] A. J. Barnard, W. C. Broad and H. Flaschka, *The EDTA Titration*. J. T. Baker Chemical Co., Phillipsburg, N.J., 1957.
[6] J. S. Fritz, R. T. Oliver and D. J. Pietrzyk, *Analyt. Chem.*, 1958, **30**, 1111.
[7] J. S. Fritz, W. J. Lane and A. S. Bystroff, *ibid.*, 1957, **29**, 821.
[8] E. Wanninen and A. Ringbom, *Analyt. Chim. Acta*, 1955, **12**, 308.
[9] J. S. Fritz, J. E. Abbink and M. A. Payne, *Analyt. Chem.*, 1961, **33**, 1381.
[10] F. J. Welcher, *The Analytical Uses of Ethylenediaminetetra-acetic Acid*. Van Nostrand, Princeton, N.J., 1958.
[11] C. W. Sill and H. Peterson, *Analyt. Chem.*, 1952, **24**, 1175.
[12] P. B. Sweetser and C. Bricker, *ibid.*, 1953, **25**, 253.
[13] R. Oesper and J. J. Klingenberg, *ibid.*, 1949, **21**, 1509.

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KOMPLEXOMETRISCHE BESTIMMUNG DES KUPFERS IN KUPFERERZEN UND KONZENTRATEN

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Zusammenfassung—Kupfer wird von einer Reihe von Metallen abgetrennt, indem es in salz-, schwefel-oder salpetersaurer Lösung in einem mit Bleifeilspänen gefüllten Reduktor zementiert wird. Das Kupfer wird mittels Wasserstoffperoxyd enhaltender Schwefelsäure aus der Säule gelöst und im Eluat komplexometrisch bestimmt.

DIE Bestimmungsmethode beruht auf der Zementation von Kupfer an der Oberfläche von Bleifeilspänen, die in eine Reduktionssäule (Bürette) eingefüllt sind, Lösen des Kupfers in verdünnter, Wasserstoffsuperoxyd enthaltenden Schwefelsäure, und anschliessender Titration mit Komplexon III. Als Indikator wird Murexid oder Xylenolorange verwendet. Die Titration mit Murexid erfolgt in schwach ammoniakalischem Medium, pH 8, die mit Xylenolorange in schwach saurem Medium, pH 5–5, 7.

Die von uns vorgeschlagene Methode ermöglicht es Kupfer schnell und vollständig von einer Reihe Kationen zu trennen: Eisen, Aluminium, Zink, Kadmium, Mangan, Kobalt, Nickel, Zinn, Titan, Chrom, Kalzium, Magnesium, Barium u.a., die ein kleineres Normalpotential haben als Blei und deshalb nicht ausgefällt werden.

Einige Elemente mit höherern Abscheidungspotential als Blei, z.B. Wismut, Silber u.a. stören nicht bei der Bestimmung von Kupfer da sie während des Titration des zweiwertigen Kupfers mit Komplexon entweder hydrolysieren oder keine stabilen Komplexverbindungen bilden. Während des Durchlaufens der Probelösung durch die Reduktionssäule wird dreiwertiges Eisen zu zweiwertigen reduziert und man kann es im Eluat oxydimetrisch bestimmen.

Die Zementation des Kupfers kann in salz-, schwefel- oder salpetersaurem Medium durchgeführt werden, wobei die Konzentration der Salz- und Schwefelsäure in der Lösung keinen wesentlichen Einfluss auf die Zementation hat. Die Konzentration der Salpetersäure darf jedoch nicht höher als 0,1 N sein.

Während die Hauptmenge des Kupfers in salzsaurem Medium entlang einer Schicht von 2–3 cm zementiert, scheidet es sich aus schwefel-oder salpetersauren Lösung (bei gleicher Durchlaufsgeschwindigkeit der Losung) entlang 6–7 cm. ab. Dies beruht auf der Passivierung der Bleifeilspäne in Gegenwart von Schwefelsäure oder auf einer Erschwerung der Reduktion von Kupfer im Beisein eines Oxydationsmittels, im gegebenen Falle-Salpetersäure.

Die Zementation des Kupfers erschwert sich jedoch wesentlich beim gleichzeitigem Vorhandensein von Salz-und Salpetersäure. In Gegenwart von Nitrosylschwefelsäure (die bei gleichzeitiger Verdampfung von Salpeter- und Schwefelsäure entsteht) zementiert Kupfer über die ganze Länge der Säule und verbleibt teilweise in Lösung. In diesem Falle ist die Ausgangslösung bis zur Bildung dichter weisser Nebel einzudampfen, abzukühlen, mit Wasser zu verdünnen und einer zweiten Eindampfung zu unterwerfen.

Die Vollständigkeit der Zementation des Kupfers, bei Verwenden einunderselben Säure hängt von der Oberflächenaktivität der Bleifeilspäne (Korngröbe der Feilspäne) von der Dauer des Kontakts der Feilspäne mit der Lösung, d.h. von der Durchlaufgeschwindigkeit der Lösung durch die Säule und der Höhe der Bleifeilspäne in der Säule (siehe Tab. I) ab.

TAB. I.—ZEMENTATION VON KUPFER AUF METALLISCHEM BLEI IN DER REDUKTIONSSAULE*

Korngrösse der Bleifeilspäne, *mm*	Säureghalt der Lösung während der Zementation, *vol % HCL*	Schichthöhe der Bleifeilspäne, *cm*	Durchlaufsgeschwindigkeit der Lösung, *ml/min*	Kupfergehalt in der Endlösung, *mg*
0,25–1,00	5	5	25	0,05
0,25–1,00	5	5	18	0,03
0,25–1,00	5	5	12	0,005
0,25–1,00	5	7,5	18	0,01
0,25–1,00	5	7,5	12	Sp
0,25–1,00	5	10	50	0,03
0,25–1,00	5	10	35	Sp
0,25–1,00	pH4	10	50	0,04
0,25–1,00	25	10	50	0,035
0,25–1,00	50	10	50	0,03
0,25–1,00	5	12,5	55	Sp
0,25–1,00	5	15	75	Sp
1–2	5	15	75	1
1–2	5	20	75	0,28
1–2	5	20	20	0,01

* Anmerkung: Bei allen Versuchen betrug die Durchlaufmenge der Lösung 50 ml mit einem Kupfergehalt von 100 mg. Die Kupfermenge in der Lösung nach Fällung des Kupfers auf Blei ist kolorimetrisch mit Aeroflot und Natriumdiethyldithio-karbamat bestimmt.

Aus Lösungsversuchen des in der Säule auszementierten Kupfers wurde festgestellt, dass im Lösen des Kupfer am besten 200 ml 2 Vol. %-iger auf 40–50°C erwärmter Schwefelsäure, die 12–18 g/l. Wasserstoffsuperoxyd enthält, verwendet werden. Bei niedriger Konzentration von Wasserstoffsuperoxyd und bei niedriger Temperatur besteht die Gefahr unvollständigen Lösens, während bei zu hoher Konzentration oder bei Temperaturen über 50°C die Lösung in der Säule kocht, die Bleisäule sulfatisiert wird, und derart die Menge des gelösten Bleis zu gross wird.

Auf alle Fälle geht beim Lösen des Kupfers zweiwertiges Blei in die Lösung. Um die schädliche Wirkung des Bleis auszuschalten wird es in Form von in Wasser und Komplexon unlöslichem Bleimolybdat ausgefällt. Nach einer anderen Variante wird zweiwertiges Kupfer in Gegenwart von zweiwertigem Blei bestimmt; in einem aliquoten Teil bestimmt man den Gesamtgehalt von Kupfer und Blei und danach in einem anderen Aliquot das Blei.

VORBEREITUNG DES REDUKTIONSSÄULE

Mit einer grobzähnigen Feile werden Bleifeilspäne aus reinem Blei (99,99%) hergestellt. Es wird eine Korngrösse von +0,25–1 mm ausgesondert und in die einen etwa 20 m langen Wattebausch enthaltende Reduktionsbürette (Reduktor nach Jones) in einer Höhe von 10–15 cm eingeschüttet. Die Reduktionssäule wird mehrmals mit verdünnter 1:4 Salzsäure und danach mit heissen Wasser bis zum Ausbleiben einer Reaktion auf Eisen durchgewaschen. Nach jeder Analyse wird die Reduktions-

säule mit heisser 10% Ammoniumazetatlösung und danach mit heissem Wasser gewaschen, um das während der Analyse gebildete Bleisulfat herausgelösen.

Die Reduktionskolonne wird am besten unter 5% (Vol). Salzsäure aufbewahrt

ANALYSE

0,250–1 g des Ausgangsmaterials werden in einem 200-300 ml Erlenmeyerkolben mit 15–20 ml konzentrierter Salzsäure (1,19) auf der Sandbank einige Minuten erhitzt und sodann 5–10 ml konzentrierter Salpetersäure zugegeben. Die Lösung wird vollständig eingedampft. Danach wird konzentrierte Salzsäure (10 ml) zugegeben und erneut eingedampft. Der Ruckstand wird in 5 ml konzentrierter Salzsäure und 50 ml destilliertem Wasser unter Erwärmen aufgenommen.

Die Filtratlösung wird mit bestimmter Geschwindigkeit durch die Reduktionssäule geschickt. Danach wird die Säule gut mit destilleiertem Wasser und 2-mal mit 0,5% Schwefelsäurenlösung durchgewaschen.

Das zementierte Kupfer wird in 200 ml 2% (vol) Schwefelsäure unter Beigabe von 12–18 g/l. Wasserstoffperoxyd gelöst. Das Lösungsmittel wird in kleinen Portionen durch die Säule geschickt, wobei jede Portion die Säule durchlaufen muss, bevor die nächste Portion zugegeben wird. Während des Prozesses wird Sauerstoff abgeschieden, was die Durchlaufsgeschwindigkeit herabsetzt. Deshalb muss die Lösung mit Hilfe eines Wasserstrahlpumpe z.B. durch die Säule gesaugt werden.

Die erhaltene Lösung wird mit 20% Natronlauge neutralisiert wobei eine Trübung entsteht. Letztere wird in einer möglichst kleinen Menge 0,5% Schwefelsäure gelöst. Die schwachsaure Lösung wird 10–15 Min. gekocht zwecks Zersetzung des Wasserstoffssupperoxyds. Nun setzt man 5 ml 1% Ammonmolybdatlösung zu, erehitzt 2 Min. und kühlt unter flüssendem Wasser. Nun setzt man Ammoniaklösung (1:3) zu, bis ein pH-Wert von 8 erreicht ist, danach titriert mit 0,04–0,05 m Komplexon III unter Verwendung von Murexid als Indikator.

Variante—Die Kupferlösung wird in einem 250 ml Masskolben aufgefangen und mit Wasser zur Marke gebracht. Man entnimmt dem Masskolben zwei 100,0 ml Portionen und gibt sie in je einen 300 ml Erlenmeyerkolben. In einem Aliquot bestimmt man die Summe von Kupfer und Blei. Hierzu neutralisiert man zuerst mit 20% iger Natronlauge auf pH etwa 5. Sodann fügt man (je nach der zu erwartenden Kupfermenge) 5–15 ml einer auf pH 6 eingestellten 20% igen Ammoniumazetatlösung. (Urotropin kann nicht als Puffer verwendet werden, da der Endpunkt sehr unscharf wird). Nach Zusatz von Xylenolorange in fester Mischung mit Kalriumnitrat wird mit Komplexon III bis zum Farbumschlag von blau nach grün titriert.

Im zweiten Aliquot wird Blei bestimmt Hierzu neutralisiert man mit Natriumhydroxyd und setzt 20% Natriumthiosulfatlösung bis zur vollständigen Entfärbung der Lösung, zu, (zweiwertige Kupferionen werden zu einwertigen Kupferionen reduziert und in Komplex gebunden). Nach

TAB. II.—RESULTATE DER KOMPLEXOMETRISHCE KUPFERBESTIMMUNG IN KÜNSTLICHEN LÖSUNGEN

Cu gegeben, *mg*	Metall in der Probe, *mg*								Cu gefunden, *mg*
	Fe	Al	Ca	Mg	Mn	Zn	Cd	Ni	
102	—	—	—	—	—	—	—	—	102
102	—	—	—	—	—	—	—	—	102
102	200	50	—	—	25	—	—	—	102,1
102	200	50	100	25	25	50	25	15	102
53	200	50	50	25	25	50	25	15	52,9
24	200	50	50	25	25	50	25	15	24

TAB. III.—ERGEBNISSE DER BESTIMMUNG VON KUPFER IN KUPFERERZEN UND KONZENTRATEN

Verwendtes Material	Kupfergehalt in %			
	jodometrisch	elektrolytisch	polarographisch	komplexometrisch
Kupfererz	1,00	1,12	1,05	1,10
Kupferkonzentrat	3,75	3,85	—	3,90
Kupferkonzentrat	8,37	8,24	—	8,35
Kupferkonzentrat	21,43	21,30	—	21,29

Zugabe von Xylenolorange und Ammonazetatpuffer wird das Blei mit Komplexon bis zum Farbumschlag von rotviolett nach gelb titriert. Aus der Differenz der verbrauchten Komplexonmenge in der ersten und zweiten Titration errechnet man den Kupfergehalt der Ausgangsprobe.

Die Resultate der komplexonometrische Kupferbestimmung in künstlicher Lösung sowie in Kupfererzen und Konzentraten sind in Tab. II und III gegeben.

Summary—Copper is separated from a series of metals, when treated in a reductor filled with lead filings, in hydrochloric, sulphuric or nitric acid solution. The copper is extracted from the column by means of sulphuric acid containing hydrogen peroxide and is determined in the eluate complexometrically.

Résumé—Le cuivre est séparé d'une série de métaux, quand il est traité par un réducteur au plomb en solution acide chlorhydrique, sulfurique ou nitrique. Le cuivre est extrait de la colonne au moyen d'acide sulfurique contenant de l'eau oxygénée et est dosé par complexométrie dans l'éluae.

LITERATUR

[1] R. Přibil, *Komplexony v chemické analyse*, CSAV, 1957.
[2] I. Körbl, R. Přibil u. A. Emr, *Chem. listy*, 1956 **50**, 1440.

Talanta, 1962, Vol. 9, pp. 413 to 419. Pergamon Press Ltd. Printed in Northern Ireland

POTENTIOMETRIC ACID-BASE TITRATION IN ACETONE-WATER SOLUTIONS OF NITROCELLULOSE*

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Summary—The development of a method for carrying out potentiometric acid-base titrations in acetone–water solutions of nitrocellulose is described. The special problems inherent in the titration of solutions with acetone concentrations greater than 90% are discussed and an instrumental method of ascertaining the attainment of equilibrium after each addition of titrant is presented. It is concluded that the optimum conditions are a maximum concentration of 0·5% nitrocellulose in a 99·5% acetone–water solution, and that the concentration of titrant must be sufficiently high for the alteration of this ratio during the titration to be very small. The care and treatment of the glass and calomel electrodes used in this titration are described and a procedure for preparing them for future use is given. Finally, mention is made of an automatic apparatus designed to carry out titrations involving slow reactions of this kind.

INTRODUCTION

DURING some studies of the production of nitrocellulose it became necessary to determine the mineral acid content of solutions of this material in acetone–water mixtures. The mineral acid concerned was sulphuric acid at a probable concentration equivalent to about 25 ml of 0·01*N* acid in 100 ml of solution. It was essential that the acetone concentration should not fall below 70% at any stage in the titration, since precipitation of a 1% concentration of nitrocellulose would otherwise occur.

Early attempts were made by other workers to carry out these titrations, using both indicators and a glass electrode-calomel electrode system. The results obtained were unsatisfactory and conflicting, even in the absence of nitrocellulose, and they became progressively worse as the acetone concentration approached 90%. Above 90% of acetone no satisfactory results were obtained and when nitrocellulose was present in a 1% concentration no useful results were obtained with any concentration of acetone that was sufficient to keep the nitrocellulose in solution.

The measurements made with the glass electrode system, which had been used in conjunction with a Cambridge null-point pH meter, indicated a considerable amount of instability, even in the absence of nitrocellulose, and this increased with increasing acetone concentration. When 1% of nitrocellulose was present the glass electrode was seriously impaired and could only be used once.

In spite of the very great difficulties experienced in the detection of the end-point in these acetone solutions the requirements of the production process allowed no change in solvent or solution conditions. The present investigation was, therefore, undertaken to study the difficulties and to provide a satisfactory method. In view of previous experience all further lines of research were, after a few preliminary experiments, concentrated upon instrumental techniques.

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Two lines of work were considered; the potentiometric method and the use of high-frequency titration. In view of the previous work the potentiometric method was studied first and the results obtained in this study are presented in this paper.

EXPERIMENTAL

Preliminary experiments

A few experiments were first made with acetone–water mixtures of acetone concentration 70–90%, using indicators to determine the end-point of the titration. These confirmed that the results had little meaning under these conditions and all further experiments were made with a glass electrode.

Preliminary studies were carried out using 100 ml of solutions with various acetone concentrations and containing the equivalent of 25 ml of 0·01*N* sulphuric acid solution. These were titrated with

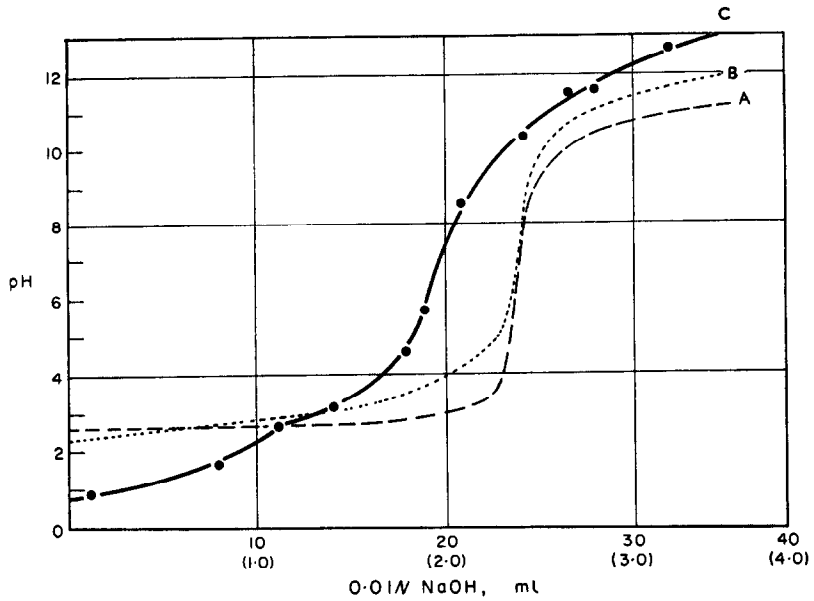


FIG. 1.—Titration curves in acetone–water mixtures, nitrocellulose absent.
– – – – – 25 ml of 0·01*N* H_2SO_4, 75 ml of water, acetone absent.
····· 25 ml of 0·01*N* H_2SO_4, 15 ml of water, 60 ml of acetone.
——— 2·5 ml of 0·01*N* H_2SO_4, 97·5 ml of acetone.
Values for NaOH in brackets refer to Curve C only.

0·01*N* sodium hydroxide solution using a glass electrode-saturated calomel electrode system in conjunction with a Cambridge null-point pH meter. The results confirmed those previously observed. Stable readings were very difficult to obtain when the acetone content was greater than 60 to 70%, because the needle of the pH meter showed a continued drift for long periods of time after each addition of reagent.

It was considered that, in solutions of this type, where the water content was small, the neutralisation reaction would certainly be slow and that this was probably the main cause of the apparent instability. The null-point instrument was therefore replaced by a Pye direct-reading pH meter and the experiments repeated. These confirmed that the reaction was very slow in reaching equilibrium and, although the direct-reading pH meter made readings easier to obtain, the response was so sluggish that long inspection was needed to ascertain when the steady state has actually been reached.

To minimise these difficulties two further modifications in technique were made. Very vigorous stirring with an electric stirrer was introduced and the potential of the electrode was fed, via the pH meter, to a Honeywell-Brown recorder. After each addition of reagent from the burette the system was allowed to stand with both the stirrer and the recorder in operation until the recorder indicated that the electrodes had reached a steady potential. The stirrer was then switched off and, after allowing for possible resulting changes in electrode potential, the reading of pH was made. The procedure was repeated until the titration curve was complete.

The quality of the titration curves obtained is illustrated in Fig. 1. Curve A represents a titration

carried out in the absence of acetone and, as expected, the curve is well-defined and equilibrium was achieved with great rapidity after each addition of alkali. Curve B was obtained with a solution which was 60% with respect to acetone. Although the end-point is well defined it is evident that deterioration of curve shape has occurred. The titration was also very much slower than that in the absence of acetone. Curve C shows the result of the titration of a solution which was 97·5% acetone. Severe deterioration of wave shape has occurred, but the slope of the curve still remains sufficiently large and well defined for the end-point to be estimated with an accuracy sufficient for the present purpose. Greater accuracy could, of course, be obtained by titrating to a specific pH value, although this would entail standardisation under carefully prescribed conditions. The neutralisation reaction in this case was extremely slow and it was, in fact, found that it was not possible to obtain a reproducible curve if the recorder method of determining the steady states was not employed. For convenience, a ten-fold reduction in the sulphuric acid concentration was made in this titration to reduce

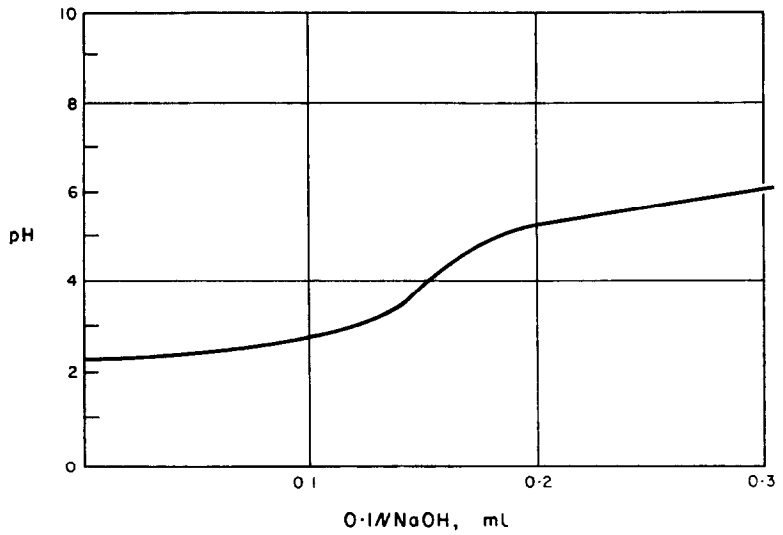


FIG. 2.—Titration of 3 ml of 0·01*N* H_2SO_4, 7 ml of water, 90 ml of acetone, containing 0·5% nitrocellulose.

the volume of sodium hydroxide solution required to effect neutralisation. In this curve the actual points have been marked to indicate the order of scatter typically obtained. A slight "hump" is apparent on the curve just before the steep rise through the end-point. This was found to be a feature of all curves of the titration of sulphuric acid with sodium hydroxide in acetone concentrations of this order.

It was found that under these conditions the acetone content could not be increased beyond 97·5%. Above this value the shape and reproducibility of the curves deteriorated very sharply.

Titration of solutions containing nitrocellulose

Application of the above method to the titration of acetone–water solutions containing nitrocellulose was next attempted. First, experiments were made with 100 ml of solutions, 90% with respect to acetone and containing 1% of nitrocellulose and 3 ml of 0·01*N* sulphuric acid solution. No satisfactory results were obtained with these solutions. The end-points were barely detectable and the reproducibility was very poor. In addition, the electrodes were badly affected and trouble was caused by the local precipitation of nitrocellulose during the addition of the alkali, unless the volumes added were kept so small that each titration was excessively lengthy even by the present standards.

Further experiments showed that it was not possible to carry out the determination in the presence of 1% of nitrocellulose and its concentration was, therefore, reduced to 0·5%. At the same time the concentration of the standard sodium hydroxide solution employed was increased to 0·1*N* so that the volume necessary to neutralise the sulphuric acid was only 0·3 ml. This had the effect of minimising the change in the acetone–water ratio as the titration proceeded.

The results obtained under these conditions were most satisfactory. Reproducible curves were obtained, but the overall pH change was very small as shown in Fig. 2.

It was concluded from these results that the acetone concentration was probably too high and experiments were, therefore, made to find an acetone–water ratio that would allow a large pH change at the end-point, while still retaining sufficient acetone to prevent precipitation of the nitrocellulose.

The results of these experiments were quite unexpected. The surprising fact emerged that for a usable titration curve with a large pH change the acetone concentration had to be increased, rather than decreased and at least 99% of acetone was shown to be necessary. Solutions of this type were, therefore, prepared using 0·3 ml of 0·1*N* sulphuric acid and 99·7 ml of acetone in a 100-ml graduated flask. Titration of this solution with 0·1*N* sodium hydroxide solution yielded curves of which that shown in Fig. 3 is a typical example. This curve has surprisingly good shape considering the very low water content although, as before, the "hump" is again present at a point just before the steep rise. The time required for each titration was considerable and extended over the whole of one working

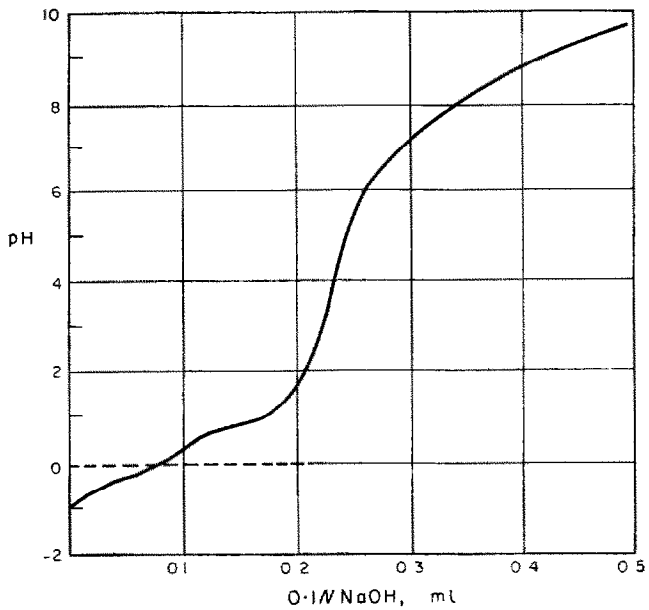


FIG. 3.—Titration of 0·3 ml of 0·1*N* H_2SO_4 and 99·7 ml of acetone, containing 0·5% nitrocellulose.

day. This was not important, however, in a fundamental study of this sort, but it is considered that reproducible results could not have been obtained without the monitoring device involving the recorder, as described above. By this method it was possible to make an addition of titrant, then leave the recorder running, returning at intervals to examine the state of the reaction.

Calibration

Finally, it was necessary to establish that, under these extreme conditions, the end-point of the titration could be used to obtain a true value for the sulphuric acid concentration in the nitrocellulose. A calibration curve was therefore prepared as follows: Aliquots of 0·1*N* sulphuric acid solution ranging from 0·1 to 0·4 ml were placed in a series of 100-ml graduated flasks. Water was added to make the volume in each case up to 0·5 ml and 0·5 g of nitrocellulose was added. Sufficient acetone was then added to each flask to dissolve the nitrocellulose and the volumes were made up to 100 ml with acetone.

These 99·5% acetone solutions were titrated with 0·1*N* sodium hydroxide solution and the results were used to construct the calibration graph shown in Fig. 4. A study of this graph shows that the relationship is linear, but that the line does not pass through zero. From this it would appear that 0·24 ml of 0·1*N* sodium hydroxide solution was equivalent to 0·3 ml of 0·1*N* sulphuric acid solution. This apparent anomaly is accounted for by the fact that the nitrocellulose sample employed had been stabilised in manufacture by the addition of sodium carbonate. The initial alkali concentration indicated by the intercept in Fig. 4 is, moreover, the amount which would be present in a normal sample of this material.

Treatment of electrodes

In view of the satisfactory nature of the above results attention was turned to the care and treatment of the glass and calomel electrodes employed. It was found that these could be used repeatedly if they were soaked in acetone after their immersion in the nitrocellulose solution. The standard treatment evolved, therefore, was to leave them to soak in pure acetone until they were required again. They were then rinsed several times with distilled water and finally soaked for 1–2 hr in a standard buffer solution.

The behaviour of electrodes that had been repeatedly used and treated in this way was examined by checking them with standard buffers of pH 4·0 and 9·15. They behaved quite satisfactorily as regards pH reading, but it was found that they were now much slower in coming to equilibrium.

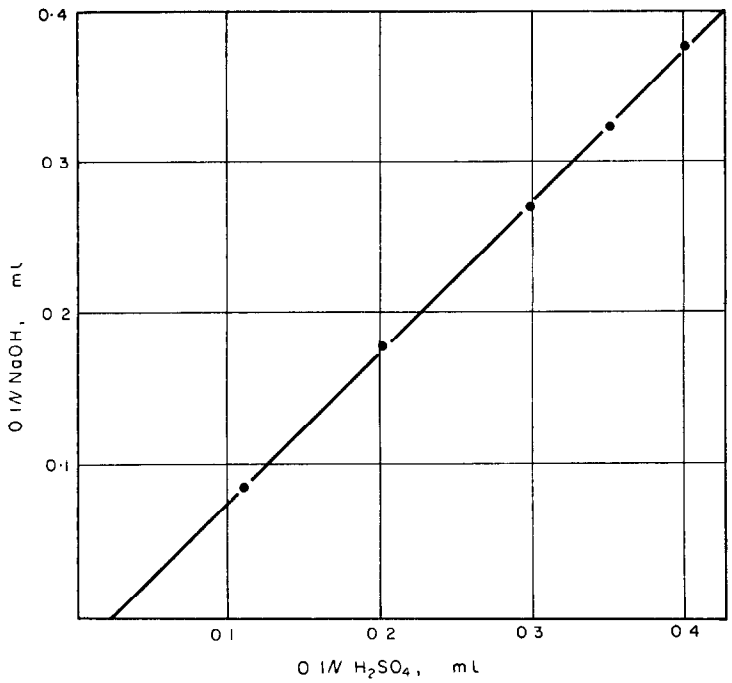


FIG. 4.—Calibration graph. Titration of sulphuric acid in 95:5 acetone:water containing 0·5% of nitrocellulose.

The possibility that the calomel electrode was responsible for the slowness of response was investigated by carrying out some titrations with the electrode replaced by a piece of chloride-treated silver foil. No conclusive results were obtained, however, and the experiments were not continued because the titration curves were much less satisfactory in shape. The reason for this is not known for certain, but it may be caused by the low concentration of chloride ions which can exist in acetone–water mixtures that are greater than 99% with respect to acetone.

CONCLUSIONS

The work described in this paper has provided the basis of a method for the determination of the acidity of solutions of nitrocellulose that have acetone concentrations greater than 90%. The conditions established are suitable for the production of titration curves of surprisingly good shape and the calibration curve obtained from them is linear over the sulphuric acid concentration range studied.

The main drawback of the method is the length of time required for each titration. No means of shortening this time is known, but the method of obtaining accurate pH readings after each addition of titrant by means of a pen recorder, relieves the strain

on the operator. Continuous observation of pH readings is unnecessary during the period taken to reach equilibrium after the addition of titrant. Even with this device, however, the method, although suitable for the present fundamental study, would not be very satisfactory for routine work. For this reason an automatic apparatus for titrations involving very slow reactions has been developed. This titrimeter may be used with any reaction which has a parameter suitable for feeding to a recorder as an electrical signal. The recorder employed has a feed-back circuit which has been used to control a motor-driven micrometer burette. The instrument has been designed to operate the burette only when a steady state has been reached and to cut if off as soon as the reaction commences again. Set in this way it will plot the titration curve of a reaction such as that described here. Alternatively, it can be arranged to slow down the speed of the micrometer burette as the pen of the recorder approaches a steady reading and to stop it at the end-point. In this way reactions, such as a titration to constant turbidity, may be carried out.

This instrument has been found to be capable of following a titration involving a slow reaction with great accuracy. It will be described in detail in a subsequent paper.[1]

Zusammenfassung—Eine Übersicht über frühere Arbeiten wird gegeben und eine Methode zur Durchführung potentiometrisches Säure-Basentitrationen in Aceton-Wasser-Lösungen von Nitrozellulose beschrieben.

Die Problematik der Titration in Lösungen mit mehr als 90% Acetongehalt werden diskutiert und eine instrumentelle Methode behandelt, die Einstellung des Gleichgewichtes nach jeder Zugabe von Titrationsmittel sichert. Es wird gefunden, wass die optimale Konzentration an Nitrozellulose 0·5% beträgt für Lösungen 99·5–0·5% Aceton–Wasser. Die Konzentration des Titrationsmittels muss hoch sein um eine zu grosse Änderung dieser Verhältnisses zu vermeiden. Behandlung der Glas und Calomelelektroden wird beschrieben. Ein automatischer Apparat zur Duchführung von Titrationen, welche auf langsamen Reaktionen beruhen, wird erwähnt.

Résumé—Après un résumé de travaux antérieurs, les auteurs dècrivent la mise au point d'une mèthode de titrage potentiomètrique acide-base de solution de nitrocellulose dans le mélange eau–acétone. Les problèmes spéciaux inhérents au titrage de solutions avec des concentrations d'acétone supérieures à 90% sont discutés et les auteurs présentent une méthode instrumentale permettant de vérifier l'obtention de l'équilibre après chaque addition de titrant. Des coubres de titrage caractéristiques et une courbe d'étalonnage sont données. Les auteurs concluent que les meilleures conditions sont une concentration maximale de 0,5% de nitrocellulose dans une solution 99,5% d'acetone-0,5% d'eau, et que la concentration de l'agent titrant doit être suffisamment élevée pour que la modification de ce rapport soit très faible au cours du titrage. Les soins et traitements à faire subir aux électrodes de verre at au calomel sont décrits, ainsi qu'une méthode de préparation de celles-ci pour un usage ultérieur. Enfin, les auteurs mentionnent un appareil conçu pour réaliser des titrages mettant en jeu des réactions lentes de ce genre.

REFERENCE

[1] L. R. Leake and G. F. Reynolds, *Talanta*, 1962, **9**, 421.

DISCUSSION OF PAPER

A. Pearson. What is the explanation for only 80% recovery of sulphuric acid in higher acetone concentrations and in the absence of nitrocellulose?

G. F. Reynolds. This apparent loss in recovery occurs only in the very high acetone concentrations (above 95%) and only under the conditions used in these titrations. In the later work with nitrocellulose present the volume of titrant added was considerably reduced and this apparent loss did not then occur. It is certain that it is caused by the large change in acetone–water ratio as the titration proceeds with consequent changes in conditions.

E. Tyrrall. Is there any difference in the time taken to reach stability after an addition at the beginning of the titration and the time required at the end of the titration? Since the concentration of reactants will be very much smaller in the latter case the time might be expected to be very much longer.

G. F. Reynolds. Little difference in time has been noticed and, since the time for equilibrium is long in any case, it has not been specially looked for. We feel that the length of time is not particularly bound up with the reactants in this system.

E. Tyrrall. Might the fact that in those titrations where nitrocellulose is present a greater concentration of acetone is required, arise from a viscosity effect? Has any attempt been made to compare the viscosity of the acetone-nitrocellulose solution of lower acetone content with that of higher acetone content?

G. F. Reynolds. No attempt has been made to measure viscosities. We do not think that the change in viscosity with increase in acetone concentration is significant.

R. J. Magee. Would there be an objection to going over completely to a non-aqueous titration, *e.g.* to the use of a non-aqueous solvent and titrating with sodium methoxide in benzene–methanol mixture? Solvolysis might explain the peculiar shape of some of the titration curves, which would be eliminated in a non-aqueous titration.

G. F. Reynolds. Unfortunately we were forced to use acetone solutions, since the method was required for the study of nitrocellulose in this medium. I agree, however, that if we had been able to use the sort of system suggested the whole titration would have been quicker and simpler and would have provided better curves. In this paper we have avoided expressing an opinion of the possible cause of the peculiar "hump" on some titration curves, as we have done no work to elucidate this problem. We agree, however, that in general, solvolysis is a likely explanation.

A. F. Williams. Has the possibility of trying a material similar to nitrocellulose been considered, since the difficulty may be in the difficulty of getting a true solution of nitrocellulose, and hence the improvement in solutions of very high acetone content?

G. F. Reynolds. This is an interesting suggestion and worth following up. We feel that it is certain that the true solution (or lack of it) of the nitrocellulose is the main reason for the improvement obtained when the acetone concentration is increased beyond 99%.

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AN AUTOMATIC-RECORDING TITRATION APPARATUS FOR USE WITH SLOW REACTIONS

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(*Received* 4 *September* 1961. *Accepted* 6 *January* 1962)

Summary—The design of an automatic-recording titration apparatus, incorporating novel features and designed for use with slow reactions, is described. A preliminary assessment of performance is presented.

INTRODUCTION

A PREVIOUS paper has described the determination of mineral acids in acetone–water solutions of nitrocellulose by potentiometric acid-base titration using a glass electrode system.[1] The acetone–water solutions employed had an acetone content greater than 95% and it was shown that, in these media, the attainment of equilibrium after each addition of titrant was so slow that a null-point pH meter could not be used. Instead, it was necessary to employ a direct-reading pH meter and to connect this to a potentiometric recorder, which was used to monitor the changes in electrode potential after the addition of titrant. Further additions were made only after the recorder chart showed that complete equilibrium had been restored.

Such a method, although very time-consuming, was quite satisfactory for the studies being made, but it was realised that for routine application an automatic apparatus was desirable. The need for such an apparatus has been generally recognised and various types of automatic titration apparatus are described in the literature.[2–7] None of these was capable of meeting the required conditions, however, and the design of a special instrument was, therefore, undertaken and is described in this paper.

EXPERIMENTAL

Apparatus Design

General considerations

Two types of titration were given particular consideration in the design of this apparatus. They were those involving partially non-aqueous media, such as that described above, and titration in aqueous media involving very dilute reactants. An example of the second kind is the titration of microgram quantities of sulphate ion with barium chloride to a constant turbidity end-point. Hillman[8] has shown that the reaction of sulphate and barium ions in dilute aqueous solutions is very slow. The special requirements of these determinations necessitated special features in the design of the apparatus as described below.

It was considered necessary that the apparatus should automatically draw a titration graph, the axes of which being the volume of titrant added and a measured parameter such as electrode potential (pH), optical density, *etc.* It was also essential that the total volume of titrant added should be kept small in order to avoid the disturbance of the concentration ratios in mixed systems. The slow addition of titrant was essential if the end-point was to be determined with accuracy and it appeared that this requirement would be met if the total time taken to complete a titration was variable within the range 30 to 180 min. The input circuit to the recorder should be such that electrical signals, derived from the titration parameter at various voltages and impedances, could be directly employed.

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An important requirement was that the rate of addition of titrant should be automatically varied with the rate of change of titration parameter, but that the volume axis of the recorder should be a linear function of the volume of titrant added.

The recorder chosen to present the titration graph was a Sunvic Model RSP2, since this instrument had design features which appeared to match the requirements of this titration apparatus. In view of the need for an accurately measured small total volume of titrant, an Agla micrometer syringe was used as the burette. The syringe employed had a capacity of 0·5 ml and could be read with an accuracy of 0·2 μl. This compares satisfactorily with the accuracy obtainable with a 50-ml burette read to 0·02 ml.

Input unit

A feature of the Sunvic recorder RSP2 is the use of interchangeable "plug-in" resistor bobbins, so that by inserting the appropriate resistance in the circuit various voltage ranges from 0·5 mV to 50 mV may be selected. This facility made the design of the input circuit much simpler. This circuit, which is shown in Fig. 1, was arranged to accept signals up to 1 V and provision was made for "backing off" any part of the signal. For input voltages not exceeding 50 mV a load of 100 Ω was applied to the source, while for input voltages between 50 mV and 1 V the operation of a switch increased the value of this load resistor to 2000 Ω. The same switch also changed the value of the total resistance of the "backing off" circuit to maintain the previous ratio (see Fig. 1). The input impedance to the recorder was fixed at 100 Ω, since by the use of a low value of this order loss of recorder sensitivity was avoided.

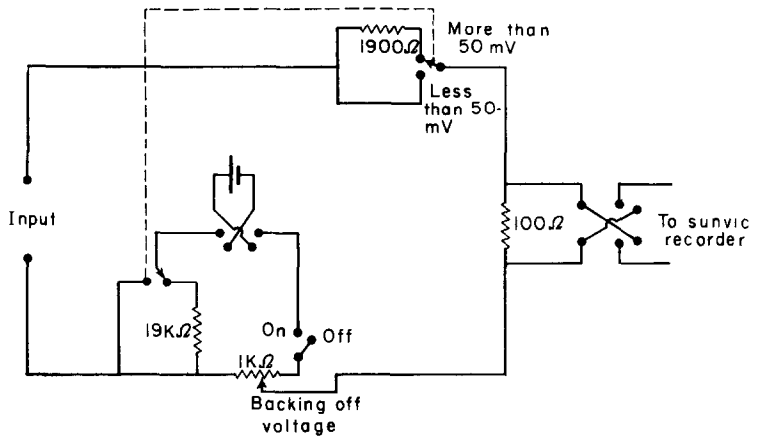


FIG. 1.—Input circuit.

Chart and burette drive

It is a fundamental principle of this instrument that the rate of addition of titrant should be variable and that the chart speed should vary similarly, so that the same length of chart would always represent the same volume of titrant irrespective of the rate of addition. To achieve this the synchronous motor fitted to the chart drive of the Sunvic recorder was replaced by an Evershed and Vignoles servo motor (generator type FO7/AR/B), together with a reduction gear of 1000:1. The arrangement of this unit and its location in the recorder is shown in Fig. 2. There was ample space for its accommodation. An identical servo motor and reduction gear was fitted to the drive of the microburette, the arrangement of which is shown in Fig. 3. Both motors were powered by the output of a single chopper amplifier, the speed of the motors being governed by the d.c. input applied to the amplifier.

Rate control system

It has already been stated that it is a fundamental principle of this instrument that the rate of addition of titrant should be variable and that the rate of chart drive should vary similarly. In order to achieve the objective completely it was also necessary to provide means whereby the speed of the burette and chart servo motors varied with the rate of change of the titration parameter being used to determine the end-point.

The characteristics required are illustrated by the series of graphs in Fig. 4. In this diagram curve A represents a typical titration curve with the end-point of the titration occurring at the point of inflection. At the end-point, the titration parameter being measured is undergoing its greatest rate of

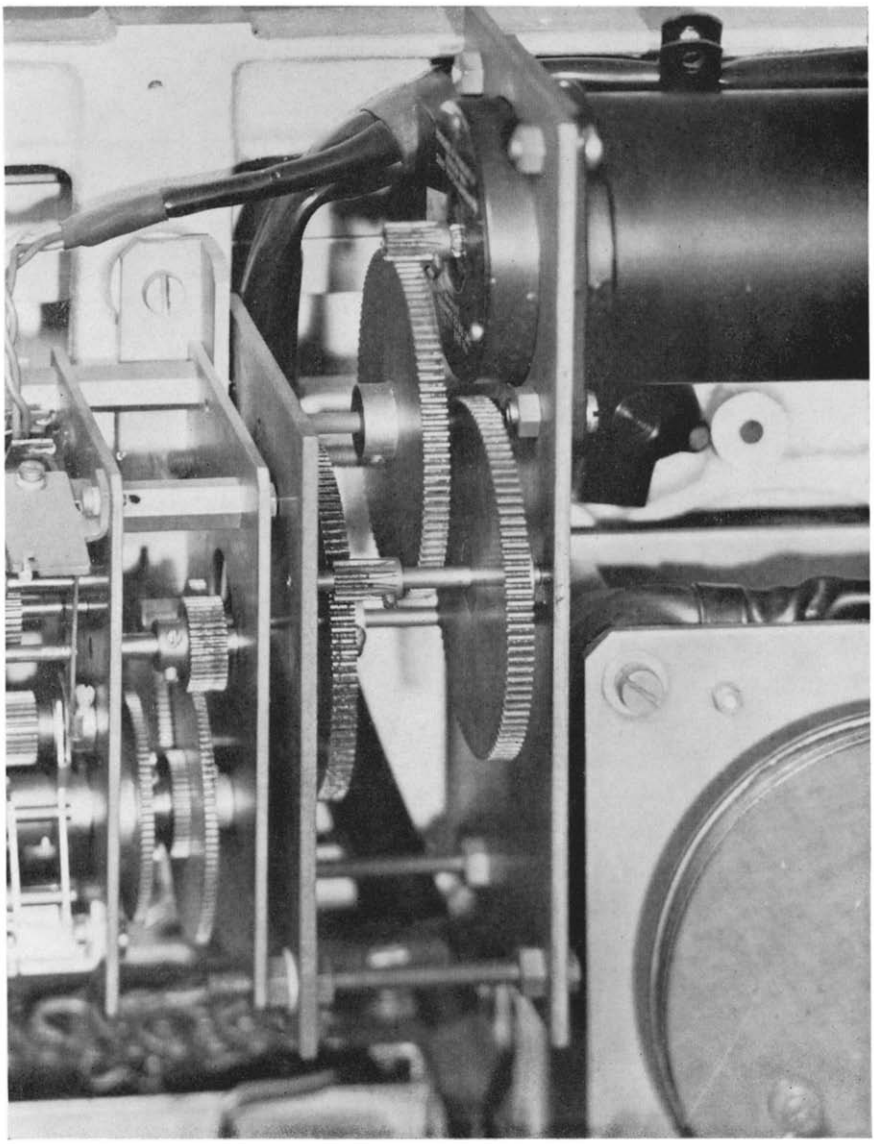


Fig. 2.—Chart drive modifications.

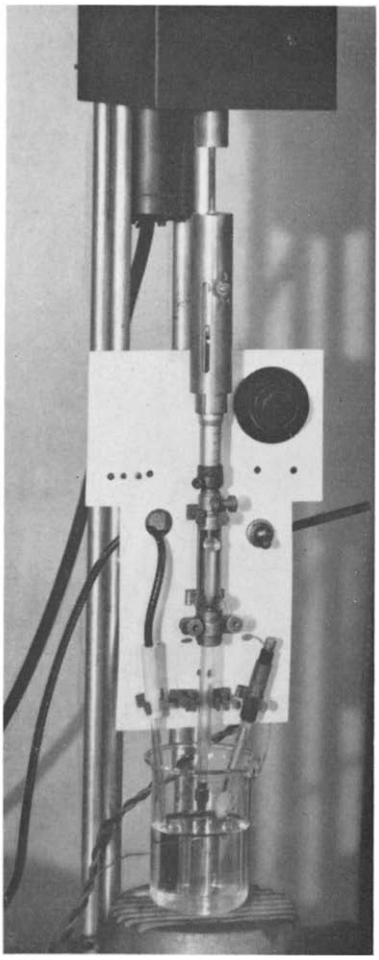


Fig. 3.—Burette unit with servomotor.

change as illustrated in curve B. Under such conditions it is necessary, for accurate end-point location, to decrease the addition of titrant at the same rate. The ideal requirement for the rate of addition of titrant is shown by curve C.

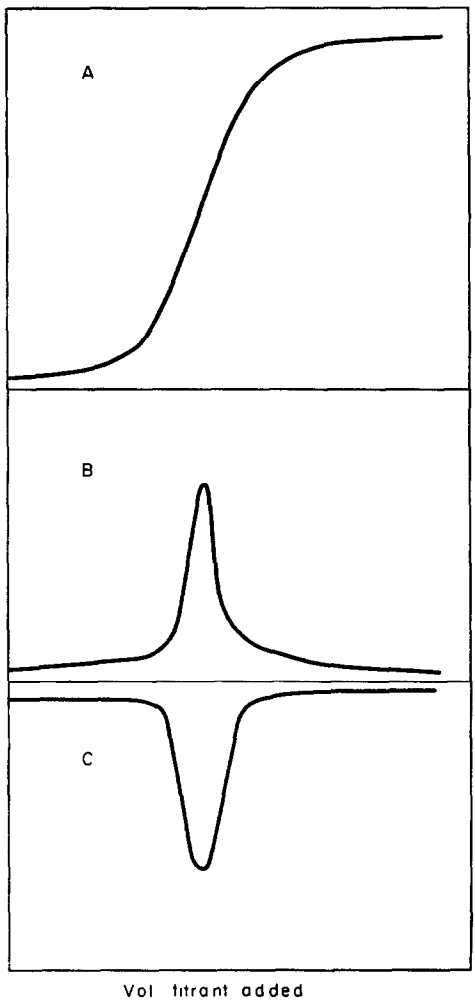


FIG. 4.—A: Titration curve.
B: Rate of change of measured parameter.
C: Rate of addition of titrant.

The signal passing through the pen amplifier of the recorder is proportional to the rate of change of the titration parameter and it was, therefore, considered that the desired rate control could best be achieved by feeding a portion of the signal in the pen amplifier to the amplifier controlling the burette and chart drives. It was evident that the phase of the signal fed back would depend on the type of titration being carried out. For a titration such as that described above the phase selected should be such that an increase in the signal through the pen amplifier would result in a decrease in the output of the burette and chart drive amplifier causing the burette and chart motors to slow down. Alternatively, for a titration such as that to constant turbidity the reverse is required since, in this case, the rate of change of the parameter (transmittance) decreases as the end-point is approached and finally becomes zero.

These requirements were met by incorporating a "feedback" loop between the amplifiers with a toggle switch for the selection of phase suitable for either of these two types of titration. Provision

was also made for variation of the rate control level, so that the magnitude of the feedback could be set to suit the determination being made. This is, of course, the factor which predetermines the amount by which the rate of addition of titrant will change with a given change in the measured parameter and hence controls the overall duration of the titration.

Apparatus Layout

The layout of the titration apparatus is given in the block schematic diagram in Fig. 5. Fig. 6 shows the apparatus as used for a potentiometric acid-base titration using a glass electrode system.

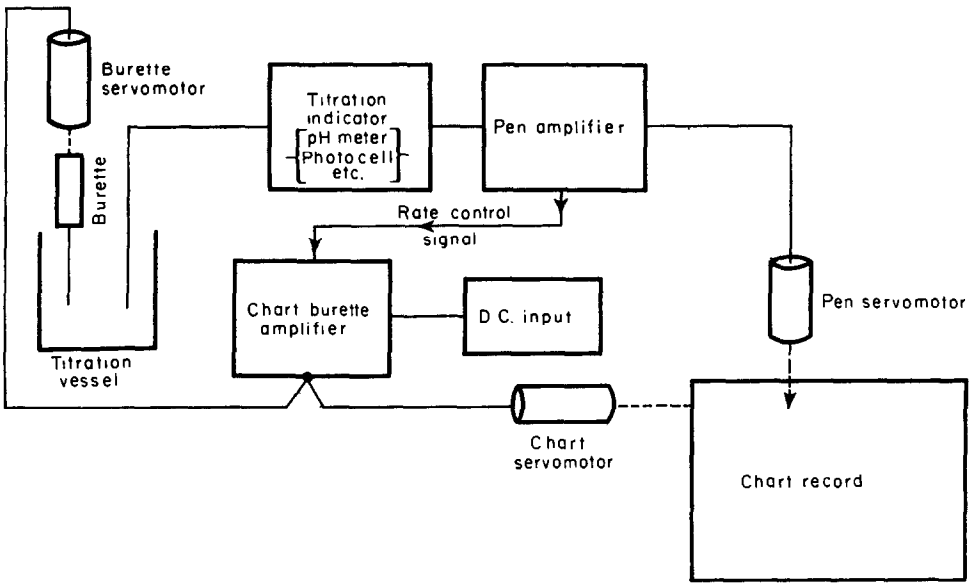


FIG. 5.—Block schematic representation of titration apparatus.

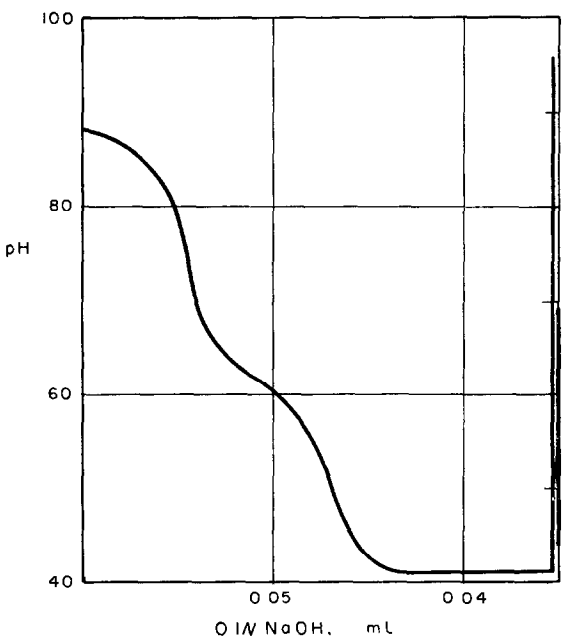


FIG. 7.—Titration of 5 ml of 0·001*N* H_2SO_4 with 0·1*N* NaOH.

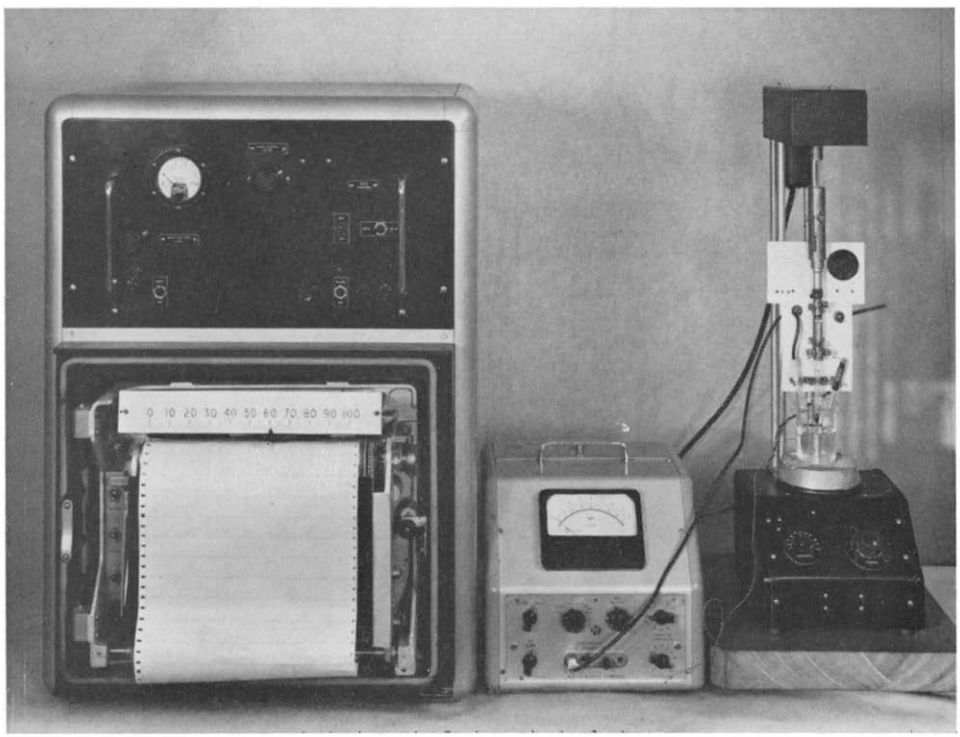


Fig. 6.—Titration apparatus (set for potentiometric titrations).

Performance

Trials with the titration apparatus showed that very satisfactory results could be obtained. It was possible to locate end-points accurately for titrations which involved rates of reaction so slow that accurate titration by even manual operation was very difficult. Both types of titration considered in this paper could be satisfactorily made. Titration curves were smooth and reproducible and the adjustment of the instrument to give optimum results was easy.

The "feedback" method of controlling chart drive and reagent addition also had the effect, not anticipated, of following very accurately the titration of fast reactions. This is illustrated by the titration of 0·001*N* sulphuric acid solution with 0·1*N* sodium hydroxide solution. Fig. 7 shows a typical titration curve for this reaction and it may be seen that two separate end-point stages were recorded, corresponding to the successive neutralisation of the two hydrogen atoms of the sulphuric acid molecule. For monobasic acids, such as hydrochloric acid, only one curve was obtained.

When applied to the determination of mineral acids in acetone–water solutions of nitrocellulose dealt with in a previous paper,[1] the results obtained were at least as good as those by very tedious, manual titration using a recorder to monitor the electrode potential. The titration curves, of course, had not the ideal shape shown in Fig. 4A and hence the requirements for the rate of change of parameter (Fig. 4B) and the rate of addition of titrant (Fig. 4C) were not completely fulfilled. Since, however, the apparatus was capable of following the change of parameter with great accuracy a satisfactory control of titration rate near the end-point was achieved. This will always be the case provided that (as in the present case) there is a distinct major change of parameter at the end-point, unmasked by other minor changes. Further studies will be reported later.

Zusammenfassung—Ein automatisches, schreibendes Titrationsgerät, welches nach neuen Geschtspunkten und besonders für den Gebrauch bei langsamen Reaktionen entwickelt wurde, wird beschrieben. Schematischer Aufbau, so wie Details der einzelnen Einheiten werden mitgeteilt. Eine vorläufige Bewertung der Eigenschaften wird gegeben.

Résumé—Les auteurs décrivent un appareil de titrage enregistreur automatique, comportant de nouvelles caractéristiques et conçu pour être utilisé dans le cas des réactions lentes. Un dessin schématique de l'instrument est donné et des détails sur les parties constituants sont fournis. Une appréciation préliminaire des performances est donnée.

REFERENCES

[1] L. R. Leake and G. F. Reynolds, *Talanta*, 1962, **9**, 413.
[2] H. M. N. H. Irving and L. D. Pettit, *Analyst*, 1959, **84**, 641.
[3] E. L. Duggan and V. L. Stevens, *Analyt. Chem.*, 1957, **29**, 8, 1076.
[4] R. Audran and D. T. R. Dighton, *J. Sci. Instr.*, 1956, **33**, 92.
[5] J. Haslam and D. C. M. Squirrell, *J. Appl. Chem.*, 1956, **9**, 65.
[6] *Idem*, *Analyst*, 1957, **82**, 511.
[7] T. K. Maple and D. N. Hume, *Analyt. Chem.*, 1956, **28**, 1116.
[8] K. Hillman, private communication.

Talanta, 1962, Vol. 9, pp. 427 to 438. Pergamon Press Ltd. Printed in Northern Ireland

AZOFARBSTOFFE ALS REAGENZIEN ZUR SPEKTROPHOTOMETRISCHEN BESTIMMUNG VON URAN(IV, VI) UND THORIUM IN LÖSUNGSMITTELGEMISCHEN*

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Zusammenfassung—In der vorliegenden Arbeit wird die Anwendung einer Reihe von Azofarbstoffen der Solochromklasse zur spektrophotometrischen Bestimmung von Uran(IV, VI) und Thorium in salzsauren methanolischen Medien beschrieben. Die angegebenen Methoden ermöglichen genaue und rasch durchführbare quantitative Bestimmungen von Mikrogrammengen dieser Elemente.

DIE hier zusammengefaßt wiedergegebenen Methoden sind das Resultat von Untersuchungen, deren Ziel es war, möglichst empfindliche und spezifische Reagenzien zur Bestimmung von Mikrogrammengen Uran und Thorium in Lösungsmittelgemischen aufzufinden und wurden im Rahmen eines Forschungsauftrages der International Atomic Energy Agency und der United States Atomic Energy Commission in diesem Institut ausgeführt.[1–8]

Die Anwendung von Azofarbstoffen als Reagenzien zur spektrophotometrischen Bestimmung von Uran und Thorium hat bis jetzt nur zur Entwicklung von wenigen Methoden geführt. *Cheng*,[9] *Gill*, *Rolf* und *Armstrong*[10] verwendeten PAN (1-2(2-Pyridylazo)-2-Naphthol) und *Pollard*, *Hanson* und *Geary*[11] (4(2-Pyridylazo)-Resorcinol) als photometrische Reagenzien zur Bestimmung von geringen Uranmengen. *Foreman*, *Riley* und *Smith*[12] zeigten, daß der Arsenazofarbstoff Thoronol (Thoron, Natriumsalz von 1-(o-Arsonophenylazo)-2-Naphthol-3,6-Disulfonsäure) nicht nur wie von *Banks* und *Byrd*[13] beschrieben zur spektrophotometrischen Bestimmung von Mikrogrammengen Thorium sondern auch zur quantitativen photometrischen Bestimmung von Uran(IV) geeignet ist. Aehnliche Ergebnisse konnten von *Fritz* und *Johnson-Richard*[14] sowie anderen Autoren[15–17] mit Neothoron (3-(2-Arsonophenylazo)-4,5-Dihydroxy-2,7-Naphthalindisulfonsäure; Arsenazo) erzielt werden. Dieser Arsenazofarbstoff kann zur spektrophotometrischen Bestimmung von Thorium und Uran(VI) verwendet werden.

Von einer großen Anzahl von untersuchten Azofarbstoffen der Solochromklasse erwiesen sich Solochromschwarz 6 BN,[8] Solochromate Fast Red 3 G[5] und Metachromschwarzblau[6] als gut geeignet zur Bestimmung von Mikrogrammengen sechswertigen Urans. Zur spektrophotometrischen Bestimmung von vierwertigem Uran haben sich die Farbstoffe Solochromschwarz 6BN[8] und Solochromate Fast Grey,[6] für Thorium Solochromschwarz WDFA,[7] Solochromate Fast Grey[6] und besonders Solochromate Fast Red[4] am besten bewährt. Der Azofarbstoff Solochromschwarz 6BN kann auch als Metallindikator zur chelatometrischen Titration von vierwertigem Uran mittels ÄDTA angewendet werden.[18] Ebenso sind in unserem Laboratorium Azofarbstoffe der Solochromklasse bereits zur Bestimmung von Gallium[19–20] (Solochromschwarz

* Herrn Univ. Prof. Dr. *Friedrich Hecht*, Vorstand des Analytischen Instituts der Universität Wien, gewidmet.

WDFA und Solochromrot ERS), Nickel[21] (Solochromrot ERS), Vanadium (Solochromate Fast Grey[22–25] und Solochromschwarz RN[26]), Titan (Solochromschwarz AS,[27] Solochrome Dark Blue B[28] und Solochromschwarz RN[29]), Zirkonium (Solochrome Violet R,[30–35] Solochromschwarz 6BN[36] und die 3 oben unter Titan erwähnten Farbstoffe[37]) und Molybdän (Solochrome Violet R[38] und die 3 oben unter Titan angegebenen Farbstoffe[39]) verwendet worden. *Khalifa*[40] verwendete Solochromate Fast Grey als Indikator für die chelatometrische Titration von Thorium mit ÄDTA.

Untersuchungen von *Korkisch*[41] und *Mitarbeitern*[42–43] hatten im übrigen gezeigt, daß die Solochromfarbstoffe in wäßriger Lösung mit Uran und Thorium keine gefärbten Komplexe bilden und teilweise eine relativ geringe Wasserlöslichkeit aufweisen. Aus diesem Grund wurde versucht auch hier wie in früheren Arbeiten[27–29] eine Komplexbildung durch Anwendung eines Methanol-Salzsäure Mediums bzw. acetatgepufferten methanolischen Mediums zu erzielen. Tatsächlich reagierte eine Reihe von Solochromfarbstoffen mit Uran und Thorium unter Bildung gefärbter Komplexe. Später wurde noch der Einfluß anderer organischer Lösungsmittel auf die Metallfarbstoffkomplexe untersucht, doch erwies sich in fast allen Fällen Methanol als den anderen Lösungsmitteln überlegen.[1–2]

Außer bei den Bestimmungen von Thorium und Uran mit Solochromate Fast Red,[4–5] die durch relativ wenige Fremdionen gestört werden, ist es in den meisten Fällen nötig, störende Fremdionen vor der spektrophotometrischen Bestimmung abzutrennen, wofür in unserem Laboratorium eine Reihe von Ionenaustauschmethoden entwickelt worden sind.[44–56] Diese, mit den stark basischen Anionenaustauschern Dowex 1, $\times 8$[51–56] und Amberlite IRA-400[44–48,50] sowie dem stark sauren Kationenaustauscher Dowex 50[49,50,52] durchführbaren Trennungen, die zum Teil ebenfalls auf Grund von Untersuchungen in mineralsauren, gemischt wäßrigen alkoholischen Lösungen[57–63] entwickelt wurden, erlauben eine rasche und quantitative Abtrennung praktisch aller, die photometrische Endbestimmung von Uran und Thorium störenden Fremdionen, wodurch eine allgemeine Abwendbarkeit (siehe Abschn. II.) der beschriebenen spektrophotometrischen Methoden ermöglicht wird.

SPEKTROPHOTOMETRISCHE BESTIMMUNG VON URAN(IV UND VI) UND THORIUM MIT SOLOCHROMFARBSTOFFEN

1. *Bestimmung von Thorium mit Solochromschwarz WDFA*[7]

(A) *Eichkurven, Empfindlichkeit und Genauigkeit der Methode*

Die Meßlösungen enthielten 0 bis 500 μg Thorium, 0,2 ml 1 n Salzsäure plus 0,8 ml 1 n Salzsäure (Abb. 1, Kurve 1) bzw. 0,8 ml 2,5 m Natriumacetatlösung (Abb. 1, Kurve 2), 2 ml 0,05% ige methanolische Farbstofflösung und den auf 10 ml fehlenden Rest Methanol. Die rein salzsauren Lösungen wurden bei 545 nm, die acetathaltigen Meßlösungen bei 530 nm gegen eine korrespondierende Reagensblindlösung gemessen. Abb. 1 zeigt, daß in beiden Fällen das Beer'sche Gesetz bis 200 μg Thorium/10 ml Meßlösung gilt. Die Empfindlichkeit der Methode[7] in rein salzsaurer Lösung beträgt 0,4 ppm, in acetatgepuffertem Medium 0,2 ppm. Die Wiederholstreuung im Bereich von 10 bis 200 μg/10 ml betrug $\pm$ 2 bis 4% (relativ).

(B) *Einfluß von Fremdionen*

Praktisch alle Kationen außer den Alkalien und alle Anionen außer Chlorid und Nitrat stören die Bestimmung, weshalb der Anwendung dieser Methode eine quantitative Trennung des Thoriums von allen Störionen vorausgehen muß, die allerdings mittels Ionenaustausches relativ leicht durchgeführt werden kann[51,52,54]

(C) *Arbeitsvorschrift*

(Ist die thoriumhaltige Lösung ein Eluat nach einer Säulenoperation[51,52,54] so muß zunächst auch die letzte Spur organischer Substanz zerstört werden. Dies erfolgt am besten durch Behandeln mit

Wasserstoffperoxyd und konz. Salzsäure in der Kälte mit nachfolgendem Eindampfen.[51,54] Der Rückstand wird in einem bestimmten Volumen 1 n Salzsäure aufgenommen).

(a) *In salzsaurer Lösung:* Aus der 1 n salzsauren thoriumhältigen Lösung wird ein Aliquot von 1 ml, das 10 bis 200 μg Thorium enthalten soll, entnommen und in einen 10-ml-Meßkolben gebracht. Nun werden 2 ml 0,05% ige methanolische Farbstofflösung hinzugefügt und der Kolben mit Methanol aufgefüllt. Die Lösung wird bei 545 nm gegen eine Reagensblindlösung spektrophotometriert und dann mittels Kurve 1 der Thoriumgehalt ermittelt.

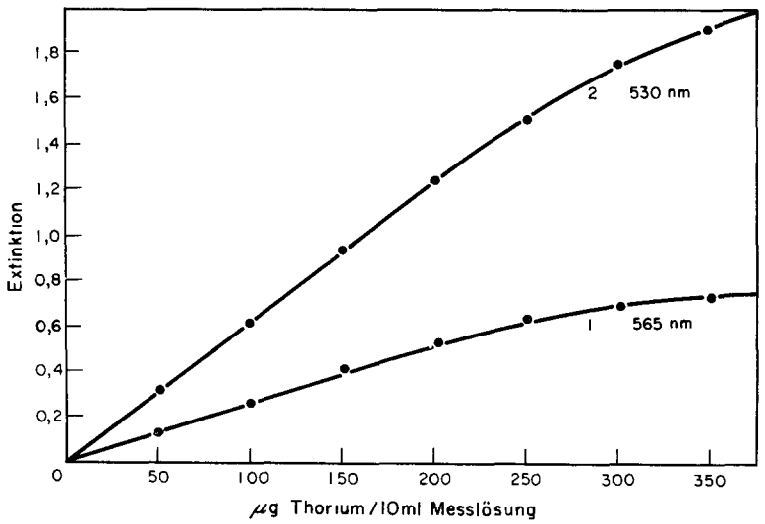


ABB. 1.—E ichkurven zur Bestimmung von Thorium mit Solochromschwarz WDFA. 1- in saurer Lösung: 2- in acetatpufferter Lösung

(b) *In acetatgepufferter Lösung:* Aus einer 1 n salzsauren thoriumhaltigen Lösung wird ein 0,2 ml Aliquot entnommen, welches 5 bis 200 μg Thorium enthalten soll und in einen 10-ml-Meßkolben gebracht. Nun werden 0,8 ml 2,5 m Natriumacetatlösung, sowie 2 ml 0,05%ige methanolische Farbstofflösung zugesetzt und mit Methanol auf 10 ml aufgefüllt. Die Extinktion wird bei 530 nm gegen eine Reagensblindlösung gemessen und mit Kurve 2 verglichen. Die Extinktion aller Meßlösungen (a) und (b) bleibt 12 Stunden konstant.

2. *Bestimmung von Uran*(IV) *mit Solochromschwarz 6BN*[8]

(A) *Eichkurven, Empfindlichkeit und Genauigkeit der Methode*

Die Meßlösungen enthielten 50 μg bis 1.000 μg Uran(IV), 1 ml 1 n Salzsäure, 2 ml 2,5 m Natriumacetatlösung, 2 ml 0,35%ige methanolische Farbstofflösung, (bzw. für Kurve 2 2 ml gesättigte glykolische Farbstofflösung) und wurden mit Methanol (bzw. für Kurve 2 mit Glykol) auf 10 ml aufgefüllt. Die Ergebnisse der Messungen dieser Lösungen gegen entsprechende Reagensblindlösungen bei 640 nm sind in Abb. 2 (Kurve 1: Eichkurve in Methanol, Kurve 2: Eichkurve in Glykol) wiedergegeben. Das Beer'sche Gesetz gilt in Bereich von 50 bis 1.000 μg. Uran(IV)/10 ml Meßlösung.

Die Empfindlichkeit der Methode beträgt 1 ppm, doch ist die Bestimmung von weniger als 50 μg Uran(IV)/10 ml nichtznempfehlen, da in diesem Gebiet starke Abweichungen von der Linearität auftreten. Im Konzentrationsbereich von 50 bis 1.000 μg U(IV)/10 ml beträgt die Wiederholstreuung ± 3 bis 5% (relativ).

(B) *Einfluß von Fremdionen*

Es wurden die Kationen Mg, Ca, Sr, Ba, Zn, Cd, Al, Sn(II), Pb(II), Ti(IV), Zr, Th, Bi(III), V(V), Cr(III), Mo(VI), U(VI), Mn(II), Fe(III), Ni, Co, La, Pr, Nd, Yb, Ce und Cu(II) sowie die Anionen, Chlorid, Jodid, Nitrat, Sulfat, Phosphat, Fluorid und Ascorbinsäure untersucht.

Die Meßlösungen enthielten: 500 μg Uran(IV), 1 mg eines der oben angeführten Kationen (als Chlorid oder Sulfat) bzw. 5 mg (bei Chlorid 50 mg) eines der Anionen (alle als Kaliumsalze, nur Fluorid als Natriumsalz), 1 ml 1 n Salzsäure, 2 ml 2,5 m Natriumacetatlösung, 2 ml 0,35%ige methanolische Farbstofflösung und den auf 10 ml fehlenden Rest Methanol. Diese Lösungen wurden gegen eine Reagensblindlösung bei 640 nm spektrophotometriert und die Extinktionen mit der

Extinktion einer Lösung, die nur 500 µg Uran(IV) aber keine Fremdionen enthielt verglichen. Es störten nicht: Mg, Ca, Sr, Ba, Cd, Pb(II), La, Pr, Nd, sowie Chlorid, Jodid, Fluorid, Sulfat und Ascorbinsäure. Alle anderen Ionen störten stark und müssen daher vor der spektrophotometrischen Bestimmung abgetrennt werden, wozu man sich einer Ionenaustauschoperation bedienen kann.[47,48,53,55]

(C) *Arbeitsvorschrift*

Die uranhältige Lösung (meist ein Eluat nach einer Säulenoperation)[47,48,53,55] wird in eine Quarzschale gebracht, am Wasserbad eingedampft und der Rückstand kurz geglüht. Das Uranoxyd wird in einigen ml 6 n Salzsäure gelöst und die Lösung nochmals auf dem Wasserbad eingedampft. Der Rückstand wird portionenweise in insgesamt 10 ml 10 n Salzsäure aufgelöst und zugleich in einen 100-ml-Meßkolben übergeführt. Darauf wird die Quarzschale noch mit 5 bis 10 ml dest. Wasser ausgespült. Zu der Uranlösung im Meßkolben wird 1 g metallisches Zink in Form von Granalien zugesetzt und die Reduktion des 6-wertigen Urans zum 4-wertigen in der früher beschriebenen Wiese (Abschn. 2) durchgeführt. Nach erfolgter Reduktion wird die Flüssigkeit, welche zum Waschen der Quarzschale verwendet worden war, zu der Uranlösung hinzugefügt und der Meßkolben mit dest. Wasser aufgefüllt. Nun wird ein 1 ml Aliquot der Uran(IV)-Lösung mit einem Gehalt zwischen 50 und 1.000 µg Uran in einen 10-ml-Meßkolben gebracht. Nach Zugabe von 2 ml 2,5 m Natriumacetatlösung und 2 ml der 0,35%igen Farbstofflösung wird mit Methanol aufgefüllt und danach die Extinktion bei 640 nm gegen eine Reagensblindlösung gemessen. Der Urangehalt der Meßlösung errechnet sich mit Hilfe der Eichkurve 1 in Abb.2.

Die Extinktion der Meßlösung bleibt 24 Stunden konstant.

3. *Bestimmung von Uran*(VI) *mit Solochromschwarz 6BN*[8]

(A) *Eichkurve, Empfindlichkeit und Genauigkeit der Methode.*

Die Meßlösungen enthielten: 0 bis 150 µg Uran(VI), 1 ml 1 n HCl, 1,5 ml 10%ige methanolische

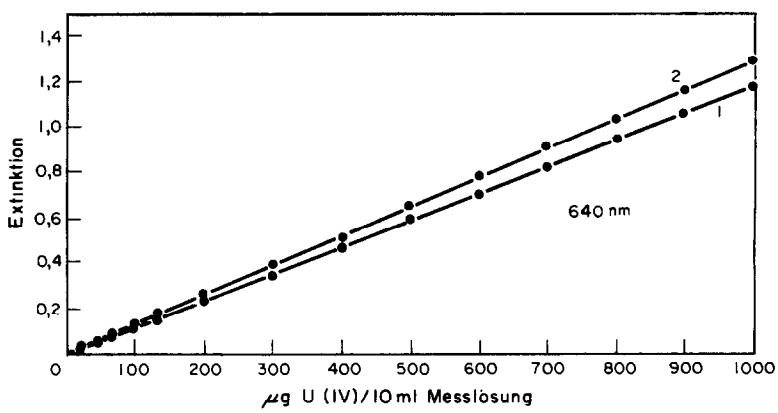


ABB. 2.—Eichkurven zur Bestimmung von Uran(IV) mit Solochromschwarz 6BN.

Zinkacetatlösung, 3 ml 0,35%ige methanolische Farbstofflösung und den auf 10 ml fehlenden Rest Methanol. Die Messung der Extinktion gegen eine Reagensblindlösung bei 640 nm ergab die in Abb. 3 gezeigte Eichkurve, aus der hervorgeht, daß das Beer'sche Gesetz von 0 bis 100 µg Uran-(VI)/10 ml Gültigkeit besitzt.

Die Empfindlichkeit der Methode ist 0,4 ppm, die Wiederholstreuung im Konzentrationsbereich von 10 bis 100 µg Uran(VI) beträgt maximal ±5% (relativ). Bei kleineren Konzentrationen streuen die Ergebnisse bis zu mehr als ±10% (relativ).

(B) *Einfluß von Fremdionen*

Es stören die gleichen Ionen, die auch die Bestimmung von Uran(IV) mit Solochromschwarz 6BN stören, doch kann man Zirkonium und Thorium mit ÄDTA maskieren. Alle anderen störenden Ionen müssen vor der spektrophotometrischen Bestimmung abgetrennt werden.

(C) *Arbeitsvorschrift*

Die uranhältige Probelösung wird in einer Quarzschale auf dem Wasserbad eingedampft, kurz geglüht und der Glührückstand mit einigen ml 6 n Salzsäure nochmals eingedampft. Nun wird 1 ml

1 n Salzsäure in die erkaltete Quarzschale einpipettiert und dieselbe unter gelgentlichem Umschwenken 10 Minuten stehen gelassen. Darauf wird mit insgesamt 5 ml Methanol portionenweise der Inhalt der Quarzschale in einen 10-ml-Meßkolben übergeführt. Nach Zusatz von 1,5 ml der 10%igen methanolischen Zinkacetatlösung und 2 ml 0,35%iger methanolischer Farbstofflösung wird mit Methanol aufgefüllt und die Extinktion gegen eine analog bereitete Reagensblindlösung bei 640 nm gemessen. Der Urangehalt der Meßlösung ergibt sich aus der Eichkurve (Abb. 3.).

Die Extinktion der Meßlösungen bleibt 24 Stunden konstant. Die Reihenfolge der Reagenzienzugabe muß eingehalten werden.

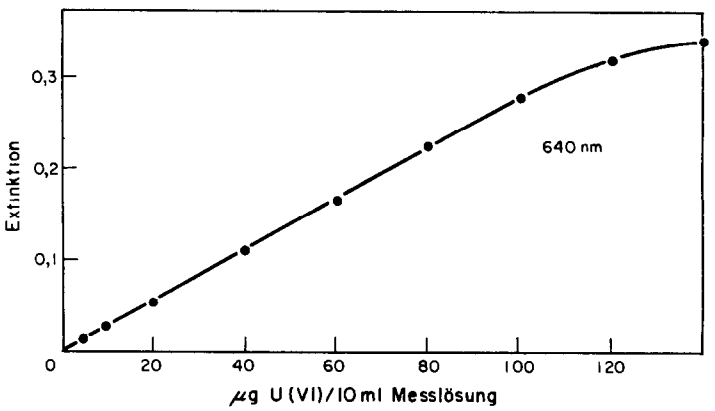


ABB. 3.—Eichkurve zur Bestimmung von Uran(VI) mit Solochromschwarz 6BN.

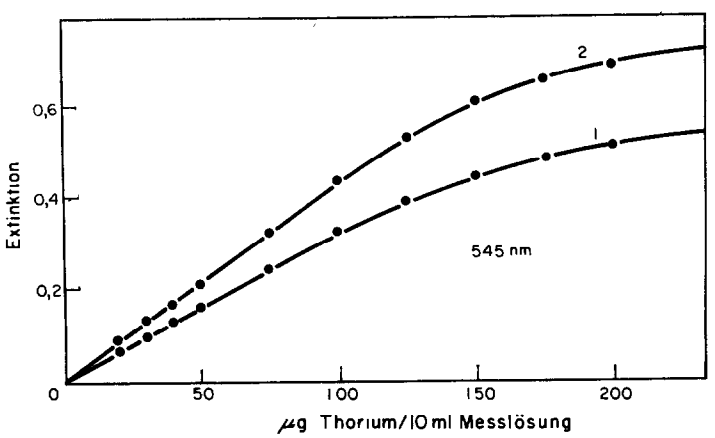


ABB. 4.—Eichkurven zur Bestimmung von Thorium mit Solochromate Fast Grey.

4. *Bestimmung von Thorium mit Solochromate Fast Grey*[6]

(A) *Eichkurve, Empfindlichkeit und Genauigkeit der Methode*

Die Meßlösungen enthielten 0 bis 200 mg Thorium, 1 ml 1 n Salzsäure, 1 ml 0,25%ige methanolische Farbstofflösung und den auf 10 ml fehlenden Rest Methanol. Diese Lösungen wurden gegen eine Reagensblindlösung bei 545 nm gemessen, wobei die in Abb. 4 gezeigte Kurve 2 erhalten wurde. Kurve 1 wurde erhalten, wenn die Meßlösungen außer den oben angegeben Reagenzien noch je0, 1 ml einer 5%igen Ascorbinsäurelösung und einer 2 m Ammoniumrhodanidlösung (zur Maskierung von Spuren Eisen und Kupfer, siehe (B)) enthielten. Das Beer'sche Gesetz gilt in beiden Fällen von 0 bis 100 µg Thorium/10 ml. Die Empfindlichkeit der Methode errechnet sich zu 0,25 ppm (Kurve 1) bzw. 0,29 ppm (Kurve 2), die Wiederholstreuung im Konzentrationsbereich von 5 bis 100 µg Thorium/10 ml wurde mit ±5 bis 7% (relativ) ermittelt.

(B) *Einfluß von Fremdionen*

Es wurden die Kationen Mg, Ca, Sr, Ba, Zn, Cd, Hg(II), Al, Sn(II), Pb(II), Zr, Bi(III), V(V), Cr(III) Mo(VI), U(VI), U(IV), Mn(II), Fe(III), Co, Ni, La, Ce, und Kupfer(II) (alle als Chloride oderNitrate) und die Anionen Nitrat (Kaliumsalz), Sulfat (Natriumsalz), Jodid (Kaliumsalz), Rhodanid (Ammoniumsalz) sowie Ascorbinsäure untersucht.

Die Meßlösungen enthielten 100 μg Thorium, 500 μg des betreffenden Kations oder 1 mg eines der oben genannten Anionen, 1 ml 1 n Salzsäure, 1 ml 0,5%ige methanolische Farbstofflösung und den auf 10 ml fehlenden Rest Methanol. Die Messung der Extinktion bei 545 nm gegen eine Reagensblindlösung ergab, daß folgende Ionen nicht stören: Mg, Ca, Sr, Ba, Zn, Cd, Hg(II), Sn(II), Pb(II), Cr(III), U(VI), Mn(II), Ni, Co sowie Nitrat, Jodid, Rhodanid und Ascorbinsäure. Alle anderen untersuchten Ionen störten die Bestimmung des Thoriums stark, doch konnten die Störungen, hervorgerufen durch Eisen(III) (bis zu 1.500 μg/10 ml) und Kupfer(II) (bis zu 300 μg/10 ml) durch Zugabe von je 0,1 ml 5%iger Ascorbinsäurelösung und 2 m Ammoniumrhodanidlösung ausgeschaltet werden. Die übrigen Ionen müssen vor der spektrophotometrischen Bestimmung des Thoriums quantitativ entfernt werden.

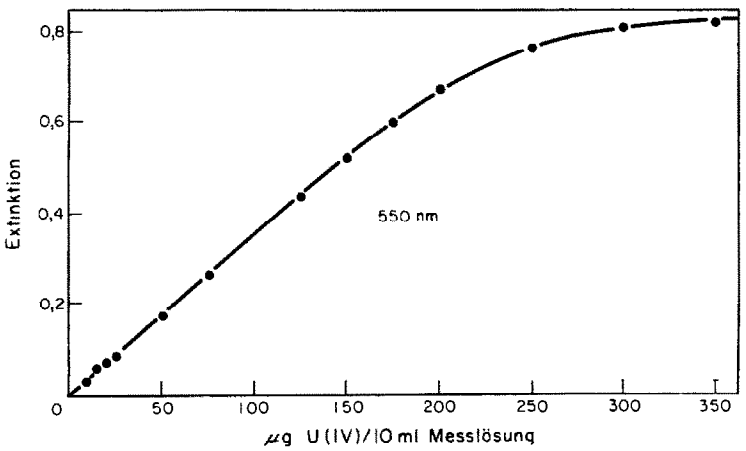


ABB. 5.—Eichkurve zur Bestimmung von Uran(IV) mit Solochromate Fast Grey.

(C) *Arbeitsvorschrift*

Die thoriumhältige Lösung (meist ein Eluat nach einer Ionenaustauschoperation[51,52,54] wird in einem 25 ml Becherglas auf dem Wasserbad eingedampft. Der Rückstand wird mit konz. Salzsäure und Wasserstoffperoxyd behandelt wie in Abschn. 11.1.C beschrieben. Der Rückstand wird in 1 ml 1 n Salzsäure aufgenommen und eine halbe Stunde stehengelassen. Darauf wird die Lösung in einen 10 ml Kolben übergeführt und das Becherglas portionenweise mit 7 ml Methanol ausgewaschen und die Waschflüssigkeit in den 10 ml Kolben hinzugefügt. Nun werden 0,1 ml 5%ige Ascorbinsäurelösung, 0,1 ml 2 m Ammoniumrhodanidlösung und 1 ml 0,5%ige methanolische Farbstofflösung in den Meßkolben einpipettiert. Nach dem Auffüllen mit Methanol wird die Extinktion bei 545 nm gegen eine Reagensblindlösung gemessen. Aus Eichkurve 1 (Abb. 8) ergibt sich der Thoriumgehalt der Meßlösung. Die Extinktion der Meßlösung bleibt 2 Stunden konstant.

5. *Bestimmung von Uran*(IV) *mit Solochromate Fast Grey*[6]

(A) *Eichkurve, Empfindlichkeit und Genauigkeit der Methode*

Die Meßlösungen enthielten 20 bis 500 μg Uran(IV) 1 n Salzsäure, 0,2 ml 2,5 m Natriumacetatlösung, 1 ml 0,5%ige methanolische Farbstofflösung und wurde mit Methanol auf 10 ml aufgefüllt. Die Resultate der Messungen der Extinktion gegen eine Reagensblindlösung bei 550 nm sind in Abb. 5 wieder gegeben. Es zeigte sich, daß das Beer'sche Gesetz über einen Konzentrationsbereich von 0 bis 150 μg Uran(IV)/10 ml befolgt wird.

Die Empfindlichkeit beträgt 0,3 ppm, doch liegt die Wiederholstreuung für die Messung kleinerer Konzentrationen als 20 μg Uran(IV)/10 ml über $\pm 10\%$ (relativ), weshalb in diesem Bereich nicht gemessen werden sollte. Im Konzentrationsbereich von 20 bis 150 μg Uran(IV)/10 ml wurde die Wiederholstreuung mit ± 7–8% (relativ) bestimmt.

(B) *Einfluß von Fremdionen*

Die Bestimmung von Uran(IV) mit Solochromate Fast Grey wird durch die gleichen Fremdionen gestört wie die Thoriumbestimmung (siehe Abschn. 4.B).

(C) *Arbeitsvorschrift*

1 ml einer 1 n salzsauren Uran(IV)-Lösung (Reduktion der Uran(VI)-Lösung siehe Abschn. 2 und 11.2.), die 20 bis 150 μg Uran enthalten soll, wird in einen 10-ml-Meßkolben gebracht. Es werden nun 0,2 ml 2,5 m Natriumacetatlösung, 1 ml 0,5%ige Farbstofflösung und Methanol bis zur 10-ml-Marke hinzugefügt. Sofort nach dem Umschütteln wird die Extinktion bei 550 nm gegen die entsprechende Reagensblindlösung (siehe Abschn. 2) gemessen. Vergleich mit der in Abb. 5 gezeigten Eichkurve ergibt den Urangehalt der Meßlösung.

Die Extinktion der Meßlösung bleibt nur 10 Minuten lang konstant und nimmt dann rasch ab.

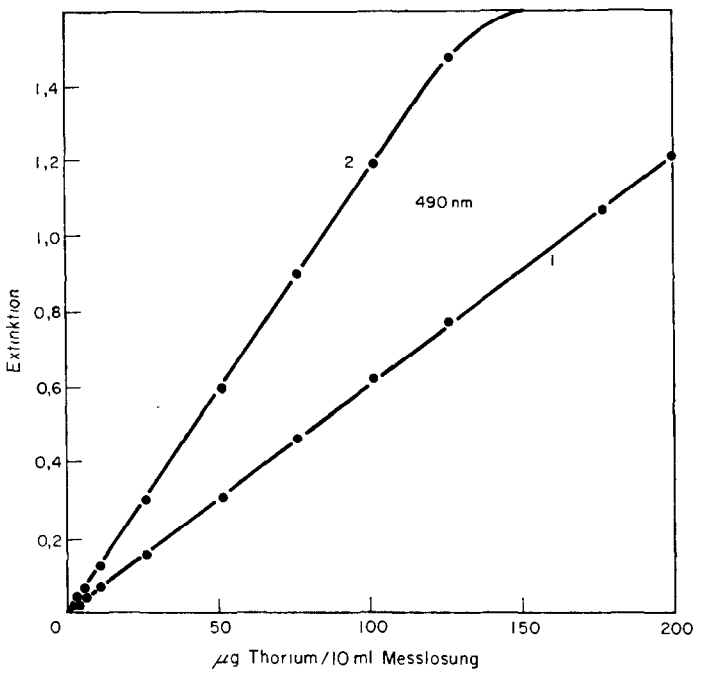


Abb. 6.—Eichkurven zur Bestimmung von Thorium mit Solochromate Fast Red.

6. *Bestimmung von Thorium mit Solochromate Fast Red*[4]

(A) *Eichkurve, Empfindlichkeit und Genauigkeit der Methode*

Die Meßlösungen enthielten 0 bis 250 μg Thorium, 1 ml 1 n Salzsäure, 0,2 ml ca. 2,5%ige methanolische Ascorbinsäurelösung, 1 ml 0,25%ige methanolische Farbstofflösung und den auf 10 ml fehlenden Rest Methanol. Diese Lösungen wurden bei 490 nm gegen eine entsprechende Reagensblindlösung spektrophotometrisch gemessen. Wie Abb. 6, Kurve 1 zeigt, gilt das Beer'sche Gesetz von 0 bis 200 μg Thorium/10 ml Meßlösung. Die Empfindlichkeit der Methode beträgt 0,16 ppm, die Wiederholstreuung im Konzentrationsbereich von 10 bis 200 μg Thorium/10 ml Meßlösung $\pm$1,5% (relativ). Von 2 bis 10 μg Thorium/10 ml traten Schwankungen von $\pm$5 bis 10% (relativ) auf. Bei Arbeiten in 5 ml Meßlösung (und halben Reagensmengen) wird Kurve 2 erhalten.

(B) *Einfluß von Fremdionen*

Es wurden die Kationen Mg, Ca, Sr, Ba, Zn, Cd, Hg(II), Al, Y, La, Yb, Pr, Nd, Ce, Sn(II), Pb(II), Ti(IV), Zr, Hf, Bi(V), V(V), Cr(III), Mo(VI), W(VI), U(VI), Mn(II), Fe(III), Co(II), Ni, Pd(II), Cu(II) und die Anionen Bromid Jodid, Fluorid, Sulfat, Nitrat, Oxalat, Citrat, Rhodanid und Ascorbinsäure untersucht. Die Meßlösungen enthielten 100 μg Thorium, 1 mg eines Kations (als Chlorid oder Nitrat) bzw. 2 mg eines Anions (als Kalium oder Natriumsalz), 1 ml 1 n Salzsäure, 1 ml 0,25%ige

methanolische Farbstofflösung und den auf 10 ml fehlenden Rest Methanol. Die Extinktion dieser Lösungen wurde gegen eine Reagensblindlösung (ohne Fremdionenzusatz) bei 490 nm gemessen.

Es stören: Fe(III), Cu(II), Ti(IV), Zr, Hf, Ce, V(V), Mo(VI) und W(VI) sowie Fluorid, Sulfat, Oxalat, Phosphat und Citrat. Durch Zusatz von 0,2 ml 2,5%iger Ascorbinsäurelösung/10 ml kann man 200 μg Fe(III) und 200 μg Cu(II) maskieren.

(C) *Arbeitsvorschrift*

Die thorium Lösung (wenn es sich um ein Eluat nach einer Ionenaustauschoperation[51,52,54] handelt, muß die Lösung zuerst behandelt werden wie in Abschn. 11.1 C beschrieben) wird in einem 25 ml Becherglas am Wasserbad zur Trockne gebracht. Der Rückstand wird in 1 ml 1 n HCl aufgenommen und unter gelegentlichem Umschütteln 15 Minuten digeriert. Darauf werden 0,2 ml 2,5%ige methanolische Ascorbinsäure zugesetzt und der Inhalt des Becherglases portionenweise mit insgesamt 7 ml Methanol quantitativ in einen 10-ml-Meßkolben gespült. Nach Zugabe von 1 ml 0,25%iger methanolischer Farbstofflösung wird mit Methanol aufgefüllt. Die Extinktion wird bei 490 nm gegen eine Reagensblindlösung gemessen und mit der Eichkurve (Abb. 6, Kurve 1) verglichen.

Die Extinktion der Meßlösungen bleibt 24 Stunden lang konstant.

7. *Bestimmung von Uran*(VI) *mit Solochromate Fast Red*[5]

(A) *Eichkurve, Empfindlichkeit und Genauigkeit der Methode*

Die Meßlösungen enthielten 0 bis 500 μg Uran(VI), 1 ml 1n Salzsäure 0,1 ml 0,1 m ÄDTA-Lösung, 1 ml 0,5%ige methanolische Farbstofflösung und 1 ml 2,5 m Natriumacetatlösung. Nach dem Auffüllen auf 10 ml mit Methanol wurde die Extinktion dieser Lösungen bei 490 nm gegen eine Reagensblindlösung gemessen und die Resultate in Abb. 7 aufgezeichnet. Aus der Kurve 1 ist ersichtlich, daß das Beer'sche Gesetz im Konzentrationsbereich von 0 bis 300 μg Uran(VI) gültig ist. Die Empfindlichkeit der Methode beträgt 0,33 ppm, die Wiederholstreuung im Konzentrationsbereich von 10 bis 300 μg Uran(VI)/10 ml $\pm 3\%$ (relativ), unter 10 μg Uran/10 ml bis $\pm 10\%$ (relativ). Bei Arbeiten in 5 ml Meßlösung (und halben Reagensmengen) wird die Kurve 2 erhalten.

(B) *Einfluß von Fremdionen*

Es wurden die Kationen Mg, Ca, Sr, Ba, Zn, Cd, Hg(II), Al, Y, La, Ce, Pr, Nd, Sn(II), Pb(II), Ti(IV), Zr, Hf, Th, Bi, V(V), Cr(III), Mo(VI), W(VI), Mn(II), Fe(III), Co(II), Ni, Pd(II), Pt(IV) und Cu(II) sowie die Anionen Bromid Jodid, Fluorid, Nitrat, Sulfat, Phosphat, Arsenat, Cyanid, Oxalat, Citrat, und Rhodanid untersucht. Die Kationen lagen durchwegs als Chloride oder Nitrate, die Anionen als Kaliumsalze mit Ausnahme von Cyanid, Arsenat und Oxalat, die als Natriumsalze vorlagen.

Die Meßlösungen enthielten je 100 μg Uran(VI), 1 mg (2 mg) des entsprechenden Kations (Anions), 0,1 ml 0,1 m ÄDTA-Lösung, 1 ml 0,5%ige methanolische Farbstofflösung und 1 ml 2,5 m Natriumacetatlösung. Sie wurden mit Methanol auf 10 ml aufgefüllt und dann ihre Extinktion bei 490 nm gegen eine Reagensblindlösung gemessen.

Es stören: Mg(schwach), Ca(schwach), Al(stark), Y, Ce, Pr, Nd, La, Ti, Zr, Th, V(V), Pd(II) (alle stark), Bi(III) (schwach), Cr(III) (schwach), Eisen(III) und Kupfer(II) (beide stark). Von den Anionen störten nur Sulfat, Bromid und Fluorid (letzteres schwach), Durch Zugabe einer 10%igen 0,1 m Kaliumcitratlösung/10 ml können 1,000 μg der Kationen Th, La, Ce, Y, Nd und Pr maskiert werden. Bis zu 100 μg Cu(II) und Fe(III) stören die Bestimmung nicht.

(C) *Arbeitsvorschrift*

Die Uran(VI)-Lösung (meist ein Eluat nach einer Ionenaustauschoperation[47,48,53,55]) wird in einer Quarzschale zur Trockne gebracht, der Rückstand kurz geglüht und nochmals mit einigen ml 6 n Salzsäure am Wasserbad eingedampft. Das Uranylchlorid wird mit 1 ml 1 n Salzsäure in der Quarzschale 15 Minuten unter gelgentlichem Umschwenken digeriert. Nach Zusatz von 0,1 ml 0,1 m ÄDTA-Lösung wird der Inhalt der Quarzschale mit insgesamt 6 ml Methanol in einen 10-ml-Meßkolben gespült. Nun werden 1 ml 0,5%ige methanolische Farbstofflösung, 1 ml 2,5 m Natriumacetatlösung und das auf 10 ml fehlende Restvolumen Methanol einpipettiert. Die Extinktion der Lösung wird bei 490 nm gegen eine Reagensblindlösung gemessen und der Meßwert mit der Eichkurve 1 (Abb. 7) verglichen.

Die Extinktion der Meßlösungen bleibt 24 Stunden konstant.

8. *Bestimmung von Uran*(VI) *mit Metachromschwarzblau*[3]

(A) *Eichkurve, Empfindlichkeit und Genauigkeit der Methode*

Die Meßlösungen enthielten in 10-ml Meßkolben: 0 bis 250 μg Uran(VI), 1 ml 1 n Salzsäure, 0,1 ml 0,1 m ÄDTA-Lösung, 1 ml 2,5 m Natriumacetatlösung, 2 ml 0,25%ige methanolische Farbstofflösung und den auf 10 ml fehlenden Rest Methanol. 15 Minuten nach dem Auffüllen und Umschütteln wurde die Extinktion dieser Lösungen bei 590 nm gegen eine Reagensblindlösung gemessen.

Wie aus Abb. 8 hervorgeht, gilt das Beer'sche Gesetz von 0 bis 200 μg Uran(VI)/10 ml Meßlösung. Die Empfindlichkeit der Methode beträgt 0,3 ppm, die Wiederholstreuung im Konzentrationsbereich von 20 bis 200 μg. Uran(VI)/10 ml $\pm 3\%$ (relativ), von 5 bis 20 μg Uran/10 ml $\pm 6\%$ (relativ).

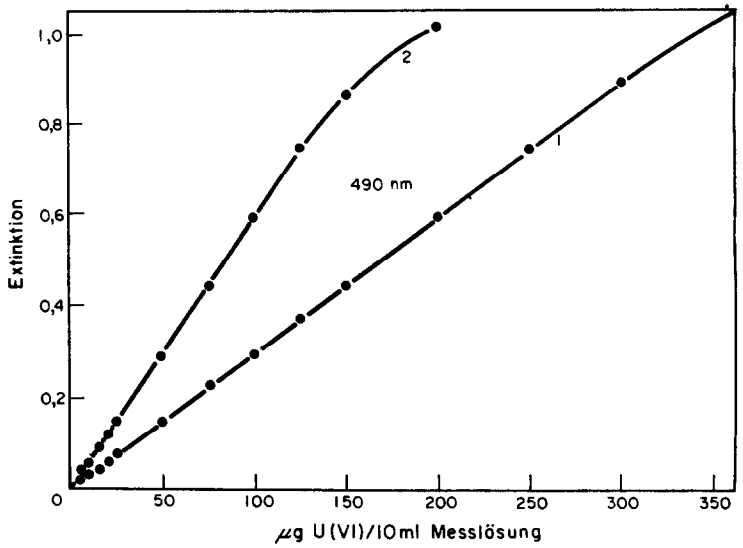


ABB. 7.—Eichkurven zur Bestimmung von Uran(VI) mit Solochromate Fast Red.

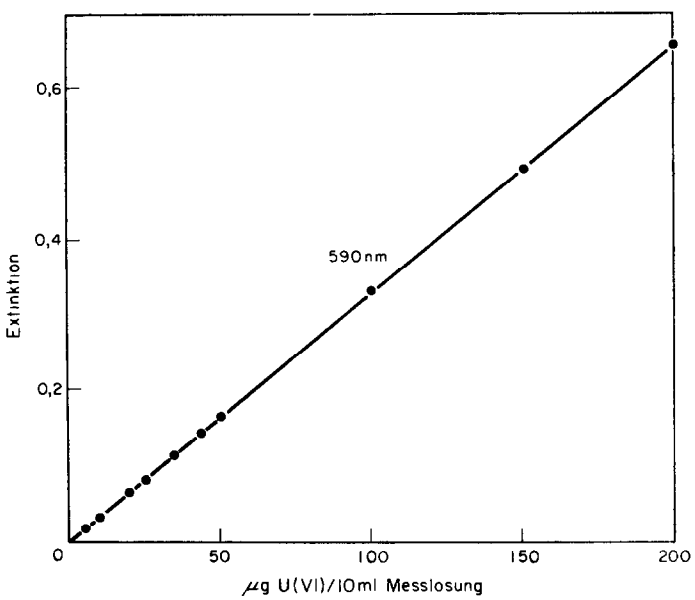


ABB. 8.—Eichkurve zur Bestimmung von Uran(VI) mit Metachromschwarzblau.

(B) *Einfluß von Fremdionen*

Es wurden die Kationen Mg, Ca, Sr, Ba, Zn, Cd, Hg(II), Cu(II), Al, La, Ce, Ti(IV), Zr, Th, Bi(III), V(V), Cr(III), Mo(VI), Mn(II), Sn(II), Pb(II), U(IV), Fe(III), Co(II), Ni(alle als Chloride oder Nitrate) und die Anionen Phosphat, Nitrat, Sulfat, Fluorid (alle als Kaliumsalze) Rhodanid (Ammoniumsalz) und Ascorbinsäure untersucht. Die Meßösungen enthielten 10 μg Uran(VI), 1 mg des Kations (oder 5 mg des Anions), 1 ml 1 n Salzsäure, 1 ml 2,5 m Natriumacetatlösung, 0,1 ml 0,1 m ÄDTA-Lösung,

2 ml 0,25%ige methanolische Farbstofflösung und das auf 10 ml fehlende Volumen Methanol. Die Extinktion der Lösungen wurde bei 590 nm gegen eine Reagensblindlösung gemessen.

Es stören nicht: Sr, Ba, Zn, Cd, Hg(II), Bi(III), Ce, Sn(II), Pb(II), Mo(VI), Co(II) sowie Nitrat und Rhodanid. Es stören schwach: Mg, Ca, Th, U(IV), Cr(III) und Mn(II). Diese Kationen sind—in Anwesenheit von ÄDTA—bis zu 500 μg tolerierbar.

Alle anderen Fremdionen mit Ausnahme der Alkalimetalle stören stark, jedoch auch Chlorid in größeren Mengen (>50 mg Natriumchlorid/10 ml Meßlösung). Die Störungen durch Cu(II) und Fe(III) können bis zu je 500 μg dieser beiden Kationen durch Zugabe von 0,1 ml 2 m Ammoniumrhodanidlösung/10 ml ausgeschaltet werden.

(C) *Arbeitsvorschrift*

Die uranhältige Lösung, die einen Gehalt von 0 bis 200 μg Uran(VI) aufweisen soll, wird mit einigen ml 1 n Salzsäure quantitativ in ein 25 ml Becherglas transferiert. War die ursprüngliche Uranlösung ein Eluat nach einer Ionenaustauschoperation[47,48,53,55], so wurde sie vorerst behandelt wie in Abschn. 11.7 C angegeben und am Wasserbad zur Trockne gebracht. Nach Zusatz von 1 ml 1 n Salzsäure wurde das Becherglas 20 Minuten unter gelegentlichem Umschütteln stehengelassen. Nun wird 1 ml 2,5 m Natriumacetatlösung, 0,1 ml 0,1 m ÄDTA- und 0,1 ml 2 m Ammoniumrhodanidlösung zugesetzt. Das Becherglas wird einige Male umgeschwenkt und der Inhalt vorsichtig in einen 10-ml-Meßkolben übertragen. Nun wird der Becher noch zweimal mit je 3 ml Methanol ausgespült und die Waschflüssigkeit ebenfalls in den 10-ml-Meßkolben gebracht. Nach Zugabe von 2 ml 0,25%iger methanolischer Farbstofflösung wird mit Methanol aufgefüllt, umgeschüttelt und nach 10 bis 15 Minuten die Extinktion bei 590 nm gegen eine Reagensblindlösung gemessen. Aus der Kurve in Abb. 12 ergibt sich der Urangehalt der Meßlösung.

Die Extinktion erreicht nach 10 bis 15 Min. den Maximalwert und bleibt dann 12 Stunden konstant.

ANWENDUNG

Um die Anwendbarkeit der beiden am wenigsten gestörten und genauesten Methoden, nämlich die Bestimmung von Uran und Thorium mittels Solochromate Fast Red[4,5], zur Ermittlung der Uran- bzw. Thoriumgehalte in natürlichen Materialien zu überprüfen, wurden eine Reihe von zusammengesetzten Mineralproben (Meeressedimente, Manganknollen) unter gleichzeitiger Zuhilfenahme von bekannten und bewährten Methoden analysiert. Thorium und Uran wurden dabei vor ihrer Endbestimmung durch Anwendung der in unserem Laboratorium für die Analyse von Meeressedimenten und sonstigen Materialien entwickelten Ionenaustauschmethoden[47–53] von den Fremdionen getrennt. Der Urangehalt der Eluate wurde dann sowohl polarographisch[44] als auch spektrophotometrisch mit Solochromate Fast Red[5] bestimmt. Die Ergebnisse dieser Messungen sind in Tab. I wiedergegeben, aus der

TABELLE I.—URANBESTIMMUNG IN MANGANKNOLLEN

	Uran, *ppm*	
Probe No*	polarographische Methode	Solochromate Fast Red Methode
1	133	136
2	130	132
3	130	135
4	265	270
5	166	170
6	115	110
7	192	200
8	205	200
9	151	155

* Die chemische und mineralogische Zusammensetzung dieser Proben wurde von Arrhenius[64] beschrieben. Ihre geochemische Bedeutung wird an anderer Stelle ausführlich diskutiert werden.

ersichtlich ist, daß die angewendete spektrophotometrische Bestimmungsmethode genauso verläßlich ist, wie die oft benutzte polarographische Uranbestimmungsmethode[44]. Letztere kann jedoch mit größerem Erfolg angewendet werden, wenn weniger als 1 μg Uran/ml Meßlösung anwesend ist.

Der Thoriumgehalt der Eluate wurde ebenfalls auf zwei Arten, und zwar mit Thoronol[13] und Solochromate Fast Red[4] bestimmt. Die Resultate dieser Analysen sind in Tab. II wiedergegeben, woraus hervorgeht, daß Solochromate Fast Red ebenso erfolgreich angewendet werden kann wie Thoronol.

TABELLE II.—THORIUMBESTIMMUNG IN MANGANKNOLLEN

	Thorium, *ppm*	
Probe No*	Thoronol Methode	Solochrome Fast Red Methode
1	12,5	12,8
2	44,5	45,0
3	12,0	12,0
4	83,3	86,0
5	63,9	64,2
6	73,5	74,0

* Siebe Tab. I.

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Summary—In the present work the application of a number of azo dyes of the Solochrome class for the spectrophotometric determination of quadri- and sexavalent uranium and thorium in hydrochloric acid-methanolic media is described. The methods developed make possible the accurate and rapid quantitative determination of microgram amounts of these elements.

Résumé—Les auteurs décrivent l'application d'un certain nombre de colorants azoïques de la série du solochrome au dosage spectrophotométrique de l'uranium et du thorium tétravalent et hexavalent en milieu acide chlorhydrique-méthanol. Les méthodes mises au point permettent des dosages quantitatifs rapides et précis de microgrammes de ces éléments.

LITERATUR

[1] J. Korkisch, Progress Report to International Atomic Energy Agency and U.S. Atomic Energy Commission under Contract No. 67/US February, 1961.
[2] J. Korkisch, *ibid.*, August, 1961.
[3] J. Korkisch und G. E. Janauer, *Z. analyt. Chem.*, 1961, **183**, 85.
[4] *Idem*, *Analyt. Chem.*, 1961, **33**, 1930.
[5] *Idem*, *Analyt. Chim. Acta*, 1961, **25**, 463.
[6] *Idem*, *Z. analyt. Chem.*, 1961, **182**, 26.
[7] *Idem*, *Mikrochim. Acta*, 1961, 880.
[8] *Idem*, *ibid.*, 1961, 537.
[9] K. L. Cheng, *Analyt. Chem.*, 1958, **30**, 1027.
[10] H. H. Gill, R. F. Rolf und G. W. Armstrong, *ibid.*, 1958, **30**, 1788.
[11] F. H. Pollard, P. Hanson und W. J. Geary, *Analyt. Chim. Acta*, 1959, **20**, 26.
[12] J. K. Foreman, C. J. Riley und T. D. Smith, *Analyst*, 1957, **82**, 89.
[13] Ch. V. Banks und C. H. Byrd, *Analyt. Chem.*, 1953, **25**, 416.
[14] J. S. Fritz und M. Johnson-Richard, *Analyt. Chim. Acta*, 1959, **20**, 164.
[15] S. Shibata und T. Matsumae, *Bull. Chem. Soc. Japan*, 1959, **32**, 279.

[16] H. Matsuyama, T. Hara und K. Koyama, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1958, **79**, 958
[17] V. I. Kuznetsov, *Zhur. Analit. Khim.*, 1958, **13**, 220.
[18] J. Korkisch, *Analyt. Chim. Acta*, 1961, **24**, 306.
[19] I. M. Ladenbauer, J. Korkisch und F. Hecht, *Mikrochim. Acta*, 1955, 1076.
[20] J. Korkisch und F. Hecht, *ibid.*, 1956, 1230.
[21] G. E. Janauer und J. Korkisch, *Z. analyt. Chem.*, 1960, **177**, 407.
[22] H. Khalifa und A. Farag, *ibid.*, 1957, **158**, 109.
[23] J. Korkisch und A. Farag, *Mikrochim. Acta*, 1958 **646**.
[24] G. E. Janauer und J. Korkisch, *Z. analyt. Chem.*, 1961 **179**, 241.
[25] *Idem*, *Talanta*, 1961, **8**, 569.
[26] G. E. Janauer, F. Tera und J. Korkisch, *Mikrochim. Acta*, 1961, 599.
[27] J. Korkisch, *Talanta*, 1961, **8**, 583.
[28] *Idem*, *Mikrochim. Acta*, 1962, 16.
[29] *Idem*, *Z. analyt. Chem.*, 1961, **182**, 92.
[30] J. Korkisch und A. Farag, *Z. analyt. Chem.*, 1959, **165**, 6.
[31] *Idem*, *ibid.*, 1959, **166**, 81.
[32] *Idem*, *ibid.*, 1959, **166**, 170
[33] *Idem*, *ibid.*, 1959, **166**, 181.
[34] J. Korkisch und Maher Osman, *ibid.*, 1959, **171**, 107.
[35] J. Korkisch, *ibid.*, 1960, **176**, 403.
[36] *Idem*, *ibid.*, 1960, **178**, 42.
[37] *Idem*, *ibid.*, 1961, **182**, 253.
[38] J. Korkisch und Maher Osman, *ibid.*, 1959, **171**, 349.
[39] J. Korkisch, *Mikrochim. Acta*, 1961, 564.
[40] H. Khalifa, *Analyt. Chim. Acta*, 1957, **17**, 194.
[41] J. Korkisch, *Dissertation*, Universität Wien, 1957.
[42] A. Farag, *Dissertation*, Universität Wien, 1959.
[43] G. E. Janauer, *Dissertation*, Universität Wien, 1961.
[44] F. Hecht, J. Korkisch, R. Patzak und A. Thiard, *Mikrochim. Acta*, 1956, 1283.
[45] J. Korkisch, A. Thiard und F. Hecht, *ibid.*, 1956, 1422.
[46] J. Korkisch, M. R. Zaky und F. Hecht, *ibid.*, 1957, 485.
[47] J. Korkisch, A. Farag und F. Hecht, *Z. analyt. Chem.*, 1958, **161**, 92.
[48] *Idem*, *Mikrochim. Acta*, 1958, 416.
[49] G. Arrhenius und J. Korkisch, *Uranium and thorium in marine materials*. Int. Oceanogr. Congr. Preprints. Ed. M. Sears 497. AAAS Wash. D.C., 1959.
[50] J. Korkisch, P. Antal und F. Hecht, *Mikrochim. Acta*, 1959, 693.
[51] J. Korkisch und P. Antal, *Z. analyt. Chem.*, 1959, **171**, 22.
[52] *Idem*, *ibid.*, 1960, **173**, 126.
[53] J. Korkisch, P. Antal und F. Hecht, *ibid.*, 1960, **172**, 401.
[54] J. Korkisch und F. Tera, *Analyt. Chem.*, 1961, **33**, 1264.
[55] F. Tera und J. Korkisch, *Analyt. Chim. Acta*, im Druck.
[56] J. Korkisch und F. Tera, *Z. analyt. Chem.*, im Druck.
[57] J. Korkisch, P. Antal und F. Hecht, *J. Inorg. Nucl. Chem.*, 1960, **14**, 247.
[58] P. Antal, J. Korkisch und F. Hecht, *ibid.*, 1960, **14**, 251.
[59] J. Korkisch und F. Tera, *ibid.*, 1960, **15**, 177.
[60] F. Tera, J. Korkisch und F. Hecht, *ibid.*, 1961, **16**, 345.
[61] F. Tera und J. Korkisch, *ibid.*, 1962, **20**, 335.
[62] J. Korkisch und F. Tera, *ibid.*, im Druck.
[63] *Idem*, *J. Chromatog.*, 1961, **6**, 530,
[64] G. Arrhenius, *Pelagic sediments. The Sea*. Interscience Publishers, New York, im Druck.

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ÜBER DIE ANALYTISCHE GRUPPE FÜR TITAN(IV) IN ORGANISCHEN REAGENTIEN

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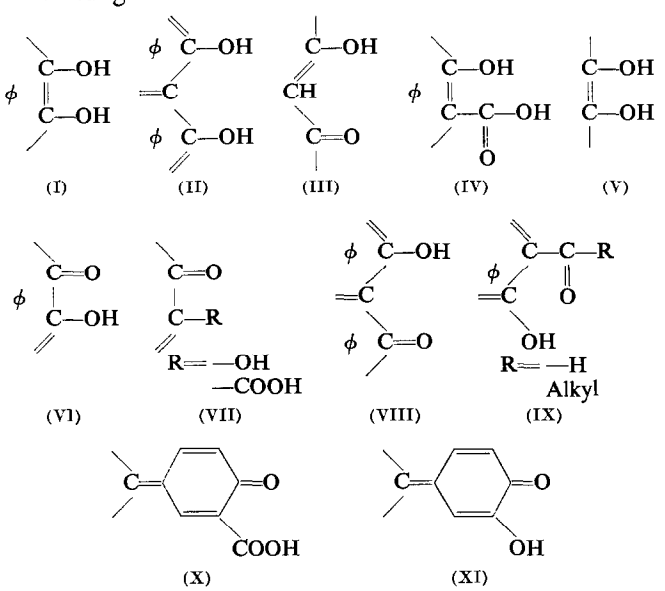
Zusammenfassung—Auf Grund theoretischer Überlegungen über analytische Donoratomgruppen in organischen Reagentien und der Bewertung zahlreicher organischen Reagentien wird eine universelle Donoratomgruppe für Ti^{IV} abgeleitet. Da diese Gruppe für Ti^{IV} nur wenig selektiv ist und eine Reihe von Ionen stören, wurden die Reaktionen von 18 analytisch wertvollsten Reagentien für Ti^{IV} eingehend studiert. Die Chromotropsäure zeigte sich für einen selektiven und empfindlichen Nachweis von Ti^{IV} bei pH 0–1 und Reagensüberschuss am besten geeignet. Der störende Einfluss einer Reihe von Ionen kann durch Reduktion mit Ascorbinsäure beseitigt werden.

DER Aufbau einer universellen analytischen Gruppe für Titan(IV) hängt mit den allgemeinen theoretischen Problemen der analytischen Atomgruppen in organischen Reagentien zusammen. Von entscheidender Bedeutung ist hier die Elektronenstruktur des Kations, die Basizität des Donoratoms des Ligandes, die allgemeinen Struktur- und sterischen Faktoren des Ligandes, die den Charakter und die Stabilität der Metall-Donoratombindung bestimmen. Es sollten dabei immer die Bindungs- und Strukturverhältnisse der ganzen Ligandenmolekül in Betrachtung genommen werden. Selten sind aber alle Fakteren und Einflüsse quantitativ bekannt, sodass der Aufbau einer solchen Gruppe überwiegend empirisch gemacht werden muss. Die Mehrzahl der resultierenden analytischen Donoratomgruppen sind im Einklang mit dem Gruppenreagentiencharakters der organischen Reagentien nur wenig selektiv und gehören gleichzeitig zu mehreren Kationen. In dieser Arbeit werden eine Reihe von Reaktionen von Ti(IV) mit organischen Reagentien kritisch bewertet und unsere älteren Resultate über analytische Gruppen für Titan(IV)[1] ergänzt. Titan(IV) bevorzugt polare Metall-Sauerstoffatombindungen an saure phenolische oder alkoholische Hydroxyle auszuüben. Dabei wird üblich der saure Proton abgespallten. Diese Bindung muss bei der Reaktion in wässrigen Lösungen durch eine weitere Bindung vorzüglich an einen zweiten Sauerstoffdonoratom oder auch an einen Stickstoff- oder Schwefelatom stabilisiert werden, sodass fünf oder sechsgliedrige Chelatringe entstehen. Färbige Produkte entstehen nur, wenn die Sauerstoffatome direkt an ein π-Elektronensystem angekoppelt sing. Ist kein π-Elektronensystem anwesend, bleiben die Lösungen farblos. Dabei kann Ti(IV) aber ebenfalls in relativ stabile Chelate gebunden werden und die Lösungen hydrolysieren bei Reagensüberschuss auch in alkalischem Medium nicht in Gegenwart von Oxalate, Tartrate, Dihydroxyweinsäure, Acetondicarbonsäure, Dihydroxyaceton.

In den wässrigen Lösungen mit Reagensüberschuss bilden sich stufenweise mehrere Chelate in Abhängigkeit von pH und Komponentenkonzentration, bei o- und peri-Diphenolen mit dem Verhältnis Ti:R = 1:1, 1:2, 1:3. Das Chelat mit Ti:R = 1:3, das sich erst in schwach saurem oder alkalischem Medium bildet, bildet sich bei schwachen Ti—O-Bindungen infolge Hydrolyse nicht mehr.[4] Die Niederschläge von

$TiO_2 . xH_2O$ sind oft mit dem färbigen Chelat verunreinigt oder können als "Lacke" betrachtet werden. Bei einer Reihe von Liganden kann man nur das einfache Chelat Ti:R = 1:1 in saurem Medium erfassen. In den äquimolaren Lösungen oder Lösungen mit kleinen Ligandenkonzentrationen sind die Reaktionsgleich-gewichte komplizierter und oft von denen in den nicht-äquimolaren Lösungen verschieden. Bei den farblosen Liganden sind die Ti(IV)-Chelate gelb oder orange gefärbt, bei der Ankoppelung an ausgedehnte π-Elektronensysteme auch rot oder violett. Mit steigender Ligandenkoordination verschiebt sich das Absorptionsmaximum hypsochrom. Über die Spektren der Ti(IV)-Chelate sind bisher nur qualitative Angaben bekannt.[2] Bei den Farbstoffen mit geeigneten Donoratomen stabilisiert sich in den Ti(IV)-Chelaten der mesomere Zustand des entsprechenden Farbstoffanion schon in saurem Medium. Damit wird der polare Charakter der Bindung Ti—O und eine geringe Beeinflussung des π-Elektronensystem durch den Kation bestätigt.[3]

Als analytische Donoratomgruppen für Ti(IV) in organischen Reagentien kommen folgende in Betrachtung:



(ϕ = aromatisches System)

Polyphenole mit einer o-Dihydroxylgruppe geben in schwach sauren Lösungen rotorange oder orange, bei pH $\geqslant$ 5 gelbe oder gelborange Färbungen, die peri-Diphenole rote oder rotviolette in saurem Medium und orange Färbungen bei pH $\geqslant$ 5, mit der Empfindlichkeit pD 5,6–6,1. (pH 2,6). Nach der Substitution eines Hydroxylprotons mit Alkyl(Guajakol, Vanillin, Vanillinsäure) sinkt die Empfindlichkeit erheblich, Veratrol reagiert nicht. Die Reaktionen dieser Reagentien find schon an anderer Stelle beschrieben worden.[4] o-Phenolcarbonsäuren, die Salicylsäure, 5-Sulfosalicylsäure, o-, m-, p-Kresotinsäuren, p-Aminosalicylsäure, β-Resorcylsäure färben die Ti(IV)-Lösungen orange in saurem Medium und gelborange bei pH $\geqslant$ 5 mit einer geringeren Empfindlichkeit, pD 5,0–5,1, bei der 1-Hydroxy-2-Naphtoesäure, 2-Hydroxy-3-Naphtoesäure mit pD 5,4, bei der Gentisinsäure mit pD 5,6. Die

Acylierung der Hydroxylgruppe hemmt die Reaktion(Acetylosalicylsäure). Noch mehr geschwächt ist die Reaktion bei den aromatischen o-Hydroxyaldehyden. Bei Salicylaldehyd entsteht eine gelbe Färbung, bei 2-Hydroxy-1-Naphtaldehyd ein oranger Niederschlag bei pH $\geqslant$ 7. Die Ti(IV). Chelate von Polyphenolen und o-Phenolcarbonsäuren können in Gegenwart von organischen Basen(Pyridin, Chinolin) bei pH 3–4 mit organischen Lösungsmitteln extrahiert werden,[5,6] ebenfalls bei pH 2–3 in Gegenwart von Tetraphenylarsoniumkation.[7,8]

5-Hydroxy-4-Pyrone geben gelbe Färbungen mit kleinen Empfindlichkeiten im Einklang mit der kleineren Stabilität der Ti-Carbonylsauerstoffbindung. Bei der Koji-Säure ist pD 3,0, Mekonsäure pD 4,4 (für beide bei pH 2,6), bei Maltol pD 3,9 (pH 1) Die Dehydracetsäure und Chelidonsäure reagieren nicht sichtbar. Die Reagentien mit einer 1,2-endiolischen Gruppe geben intensive rotorange Färbungen in saurem, Medium gelborange Färbung oder Niederschlgg bei pH $\geqslant$ 5, die Ascorbinsäure mit pD5,4, die Dihydroxymaleinsäure mit pD 5,6 (bei pH 6).

Die gelben Lösungen von Ti(IV) in Gegenwart von enolisierbaren 1,3-Diketonen hydrolysieren leicht bei pH 3. Die Empfindlichkeit ist klein, bei Acetylaceton ist pD 3,7 (pH 5). Für die Bewertung der Ti(IV)-Reaktionen dieser Gruppe von Reagentien siehe.[9] Ähnlich verhalten sich auch Derivate des Acetophenons, o-Hydroxyacetophenon und Resacetophenon mit pD 4,7 (pH 3). Von theoretischer Interesse sind auch die anomal intensive grüne Färbungen der Reaktionen der aliphatischen enolisierbaren 1,3-Diketone mit Ti(III).[9] Empfindlich aber wenig selektiv ist die Reaktion von Curcumin mit Ti(IV) bei pH 5–6. Es bilden sich rotbraune Färbung und Niederschlag mit pD 5,4 (Die äthanolische Lösung von Reagens ist bei diesem pH gelb). Äthylester der Acetessigsäure reagiert undeutlich.

Die Verbindungen mit o-oder peri-chinoider Struktur reagieren nur wenig deutlich (Phtiokol, 2-Hydroxy-1,4-Naphtochinon, Juglon). Bei Naphtazarin entsteht ein blauer Niederschlag bei pH $\geqslant$ 5 (die äthanolische Lösung des Reagenses ist rotviolett). Anomal empfindlich aber wenig selektiv sind Polyhydroxyflavone. Die Bildung oranger Färbungen und Niederschläge bei Quercetin, Rutin, Morin hat die Empfindlichkeit pD 5,9–6,1 bei pH 5.

Bei der Ankoppelung der charakteristischen Sauerstoff Donoratomgruppen an das Resonanzsystem eines Farbstoffes verliert die Reaktion mit Ti(IV) oft die Empfindlichkeit oder sie wird ganz undeutlich. Auch die Selektivität ist gering. Empfindliche Farbumschläge von orange oder braunorange nach blau bei pH 5–6 sind bei den Triphenylmethanfarbstoffen mit (X), bei Eriochromcyanin R(3,3′-Dimethyl-4′-Hydroxy-5,5′-Dicarboxy-2″-Sulfofuchson) mit pD 6,1, Chromazurol S(3,3′-Dimethyl-4′-Hydroxy-5,5′-Dicarboxy-2″,6″-Dichloro-3″-Sulfofuchson) mit pD 6,1 und Eriochromgeranol R(3,3′-Dimethyl-4′-Hydroxy-5,5′-Dicarboxy-3″-Carboxy-4″-Hydroxy-5″-Methylfuchson) der Farbumschlag nach rot mit pD 5,4. Bei Aluminon. (4′,4″-Dihydroxy-5,5′,5″-Tricarboxyfuchson) ist die Reaktion wenig empfindlich. Hematein mit der Gruppe (VII) färbt sich in Gegenwart von Ti(IV) nur wenig empfindlich von orange nach rot bei pH 2. Bei pH 5 ist die Reaktion nicht mehr deutlich und wenig selektiv.

Azofarbstoffe dei Azochromotropsäurereihe (XII) färben sich in Gegewart von Ti(IV) von orange, rot oder rotviolett nach rot, rotviolett oder blauviolett bei pH 5. Die Empfindlichkeit ist pD 4,2–4,7 für die Derivate mit R: AsO_3H_2—, COOH—, C_2H_5O—, NO_2—, OH—, SO_3H—.

TABELLE I. DIE REAKTIONEN EINIGER REAGENTIEN FÜR TITAN(IV)

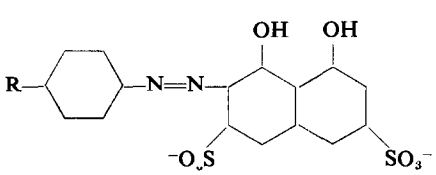
Reagens	Reaktion mit Ti(IV)	pD	Reaktionen anderer Ionen im entsprechenden pH-Bereich	Bemerkungen u. ältere Literaturangaben für die Ti(IV)-Reaktion
Chromotropsäure, Dinatriumsalz	rote Fbg.,* pH 1–3 orange Fbg., pH 5–8	6,1[a] 6,1[a]	pH 1–3 Fbgn.: Fe^{3+}, Mo^{VI}, Nb^{V}, Ta^{V}, V^{V}, Cr^{VI} Ce^{IV}, W^{VI}, $Tl^{III}(U^{VI}, Cu^{2+})$ Ndg.:** Hg^{2+}, Au^{III}, Bi^{3+}, Zr^{IV}	Festes Reagens. Siehe auch 4, 17, 18
Quercetin	rotorange Fbg., pH 3	6,1[a]	pH 3 Fbgn.: Zr^{IV}, In^{3+}, Ga^{3+}, Y^{3+}, Sc^{3+}, Tl^{III} Ndg. U^{VI}, Mo^{VI}, V^{V}, Al^{3+}, Sn^{IV}, Bi^{3+}, Th^{4+}, V^{IV}, $Hg^{II,I}$, Au^{III}, Fe^{3+}, W^{VI}, Nb^{V}, Ta^{V}, Ce^{IV}, $Pd^{2+}(Cu^{2+}, Ag^{+}, Pb^{2+})$.	Gesättigte Reagenslsg. in 20% Äthanol. Siehe auch[20]
Rutin (Quercetin-3-Rutinosid)	rotorange Fbg., pH 3	6,0[a]	pH 3 wie bei Quercetin	Gesätigte Reagenslsg. in 20% Äthanol. Siehe auch[21]
2,3-Dihydroxynaphtalin-6-Sulfonsäure, Natriumsalz	rotorange Fbg., pH 2,6 gelborange Fbg., pH $\geqslant$ 7	5,9[a] 5,9[a]	pH 2,6 Fbgn.: Fe^{3+}, U^{VI}, Mo^{VI}, Nb^{V}, Ta^{V}, V^{V}, Cr^{VI}, W^{VI}, $Bi^{3+}(Ce^{IV}, Cu^{2+})$. Ndg.: Hg^{2+}, Ag^{+}, Au^{III}, Bi^{3+}, Zr^{IV}	Gesättigte Reagens-läg. in Wasser
Protocatechualdehyd	rotorange Fbg., pH 2,6 gelborange Fbg., pH 7	5,9[a] 5,9[a]	pH 2,6 Fbgn.: Mo^{VI}, W^{VI}, V^{V}, Fe^{3+}, U^{VI}, Hg^{2+}, Cr^{VI}, $Bi^{3+}(V^{IV}, Cu^{2+})$. Ndg.: Hg^{2+}, Ag^{+}, Zr^{IV}	Gesättigte Reagenslsg. in 20% Äthanol
Brenzcatechin-3,5-Disulfonsäure, Dinatriumsalz (Tiron)	rotorange, pH 2,6 gelborange, pH 7	5,8[a] 5,8[a]	pH 2,6 Fbgn.: Fe^{3+}, Mo^{VI}, U^{VI}, Nb^{V}, V^{V}, Cr^{VI}, W^{VI}, Bi^{3+}, Cu^{2+}, Hg^{2+} (Ta^{V}) Ndg.: Hg^{2+}	Festes Reagens. Siehe auch[22,23]

Pyrogallol-4-carbonsäure	rotorange, pH 2,6	5,8[a]	pH 2,6 Fbgn.: Fe^{3+}, U^{VI}, Mo^{VI}, Nb^{V}, Ta^{V} V^{V}, W^{VI}, Cr^{VI}, Cu^{2+}, Tl^{III}. Ndg.: Hg^{2+}, Au^{III}, Bi^{3+}, Pd^{2+}, Zr^{IV}, Hg^{I}	Gesättigte Reagenslsg. in Wasser
Gallussäure	rotorange Fbg., pH 2,6	5,8[a]	pH 2,6 Fbgn.: Fe^{3+}, U^{VI}, Nb^{V}, Ta^{V}, Mo^{VI}, $V^{V,IV}$, W^{VI}, Tl^{III}, (Cr^{VI}, Cu^{2+}) Ndg.: $Hg^{I,II}$, Bi^{3+}, Au^{III}, Pd^{2+}, Zr^{IV}	Gesättigte Reagenslsg. in Wasser. Siehe auch[27]
Protocatechusäure	rotorange Fbg., pH 2,6 gelborange Fbg., pH 7	5,7[a] 5,7[a]	pH 2,6 Fbgn.: Fe^{3+}, Mo^{VI}, Nb^{V}, V^{V}, Ta^{V}, U^{VI}, Tl^{III}, W^{VI}, Hg^{2+}, Cr^{VI}, Bi^{3+} (Ce^{IV}, V^{IV}, Cu^{2}) Ndg.: Hg^{2+}, Bi^{3+}, Au^{III}, Pd^{2+}, Zr^{IV} (Th^{IV})	Gesättigte Reagenslsg. in 30% Äthanol
Hydroxyhydrochinon	rotorange Fbg., pH 2,6	5,6[a]	pH 2,6 Fbgn.: Fe^{3+}, Mo^{VI}, U^{VI}, V^{V}, W^{VI}, Nb^{V}, Ta^{V}, Bi^{3+}, Cr^{VI}. Ndg.; Ag^{+}, Cu^{2+}, $Hg^{I,II}$, Au^{III}, Pd^{2+} (Pb^{2+})	Festes Reagens, Oxydationsempfindlich
Dihydroxymaleinsäure	rotorange Fbg., pH 2,6 gelborange Fbg., pH 7	5,3[a] 5,6[a]	pH 2,6 Fbgn.: Fe^{3+}, U^{VI}, W^{VI}, Mo^{VI}, Nb^{V}, Ta^{V}, V^{V}, Cr^{VI}. Ndg.: Ag^{+}, Pd^{2+}, Au^{III}, Cu^{2+}, Tl^{III}, Zr^{IV}, Th^{IV}(Sb^{III}, La^{3+}, Pb^{2+})	Festes Reagens. Siehe auch[25]
Ascorbinsäure	orange Fbg., pH 6	5,4[a]	pH 5: Fbgn.: U^{VI}, Nb^{V}, Te^{V}, Bi^{3+}, Cu^{2+}, W^{VI}, Mo^{VI}($V^{V,IV}$), Fe^{3+}. Ndg.: Tl^{III}, Ag^{+}, $Hg^{I,II}$, Cu^{2+}, Bi^{3+}, Au^{III}, Pd^{2+}	Festes Reagens. Siehe auch[26]
5-Sulfosalicylsäure	orange Fbg., pH 2,6 gelborange Fbg., pH 5	5,1[a] 5,1[a]	pH 2,6–5 Fbgn.: Cu^{2+}, Fe^{3+}, Mo^{VI}, Nb^{V}, U^{VI}, W^{VI}, Ce^{IV}(Ta^{V}) Ndg.: Zr^{IV}	Festes Reagens. Siehe auch[27]

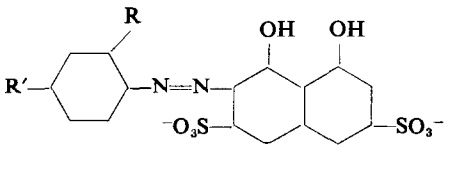
TABELLE 1 (*continued*)

Reagens	Reaktion mit Ti(IV)	pD	Reaktionen anderer Ionen im entsprechenden pH-Bereich	Bemerkungen u. ältere Literaturangaben für die Ti(IV)-Reaktion
4-(2-Pyridylazo)orcin	rotorange Fbg., pH 5	6,2[b]	pH 5 Cu^{2+}, Pd^{2+}, Bi^{3+}, $V^{V,IV}$, Tl^{III}, Mo^{VI}, W^{VI}, Zr^{IV}, Ga^{3+}, In^{3+}, Sc^{3+}, Y^{3+}, La^{3+}, S.E., Ce^{3+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, U^{VI}, $Hg^{I,II}$, Au^{III}, Fe^{3+}, Fe^{2+}, Ce^{IV}, Th^{4+}, Be^{2+}, Nb^{V}, Ta^{V}.	3 Tropfen von gesättigter wäss. Reagenslsg. in 1 ml (gelb bei pH 5)
Eriochromcyanin R	rote Fbg. oder Niederschlag. pH 6	6,1[b]	pH 6 Fbgn.: Al^{3+}, Y^{3+}, Ga^{3+}, Sc^{3+}, In^{3+}, Zr^{IV}, $V^{V,IV}$, Th^{4+}, Fe^{3+}, Cu^{2+}, U^{VI}, Nb^{V}, Ta^{V}, Mo^{VI}, $Hg^{I,II}$, La^{3+}, Bi^{3+}, Au^{III}, Pb^{2+}, (Cd^{2+})	2 Tropfen gesättigter Reagenslsg. in 20% Äthanol in 1 ml (gelborange bei pH 6)
Resoflavin (Sch. Tab. 771)	braunrote Fbg., pH 1 braunrote Fbg,. und Niederschlag pH 6	4,9[a] 6,0[a]	pH 3 Ag^{+}, Cu^{2+}, Pb^{2+}, $Hg^{I,II}$, Bi^{3+}, Fe^{3+}, U^{VI}, Zr^{IV}, $V^{V,IV}$, Th^{4+}, Mo^{VI}, W^{VI}, Ce^{IV}, Au^{III}, T^{III}, Ga^{3+}(S.E.)	Gesättigte Äthanollösung, (gelb bei pH 3) Siehe auch[28]
2-Arsonophenyl-1-azo-2-chromotropsäure, Natriumsalz (Arsenazo)	blaue, blauviolette Fbg, pH 1 blaue Fbg., pH 5	5,9[b]	pH 2–3: Fe^{3+}, U^{VI}, Zr^{IV}, Th^{IV}, V^{V}, Nb^{V}, Ta^{V}, Y^{3+}, Ga^{3+}, In^{3+}, Sc^{3+}(Be^{2+}, Ce^{3+}, Bi^{3+}, La^{3+}, Al^{3+}), Ce^{IV}	3 Tropfen gesättigter wässrigen Reagenslsg. in 1 ml (rosa bei pH 2) Siehe auch[29,30]
2-Arsono-4-Methylphenyl-1-azo-2-Chromotropsäure (Methylarsenazo)	blaue Fbg., pH 1 blaue Fbg., pH 5	5,8[b]	wie bei Arsenazo	3 Tropfen gesättigter wässriger Reagenslsg. in 1 ml (orange bei pH 1, rot bei pH 5)

[a] Die Empfindlichkeiten für einen Tropfen am Tüpfelbrett angegeben(Gesamtvolumen des Tropfens einberogen).
[b] Die Empfindlichkeiten für 1 ml Lösung im Probierglas angegeben.
* Fbg. = Färbung, ** Ndg. = Niederschlag



(XII)



(XIII)

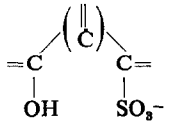
Nur bei der p-Methylphenylazochromotropsäure erreicht sie pD 4,9, bei der Phenylazochromotropsäure pD 5,1. Die Ti(IV)-Reaktionen der zweiten Azochromotropsäurereihe (XIII) sind empfindlicher. Diese Farbstoffe können als mehrzählige Ligande auftreten und stabilere Chelatbindungen ausüben. Die Farbumschläge sind von orange oder orangerot nach rot, violett oder blau. Die Empfindlichkeit ist pD 4,5–4,9 für die Derivate mit R: SO_3H—, OH—, R': H. Mit einer grossen Empfindlichkeit reagieren die 2-Arsonophenylazochromotropsäure ("Arsenazo") mit dem Farbumschlag von orangerot nach blauviolett und pD 5,9 bei pH $\geqslant$ 1, die 2-Arsono-4-Methylphenylazochromotropsäure mit dem Farbumschlag von orange nach blau und pD 5,8 bei pH $\geqslant$ 1, die 2-Arsono-4-Nitrophenylazochromotropsäure mit pD 5,3 (pH 5), die 2-Carboxyphenylazochromotropsäure mit pD 5,5 beipH 5. Stilbazo (2,2'-Disulfostilben-4,4'-bisazo-3,4-Dihydroxybenzol), MagnesonIREA (2-Hydroxy-3-Sulfo-5-Chlorphenylazo-1-Naphtol-2), Berillon IREA (1-Hydroxy-3,6-Disulfonaphtalin-1-azo-2-Chromotropsäure), Calcion IREA (2-Naphtol-1-azo-1-naphtol-2-Sulfonsäure-4.) Thorin (2-Arsonophenyl-1-azo-1-2-Naphtol-3-Sulfonsäure) reagieren mit Ti(IV) wenig deutlich oder bleibt die Reaktion ganz aus. Von den Pyridinazofarbstoffen haben ausgeprägte Farbumschläge von gelb nach rotorange bei pH 5 4-(2-Pyridylazo) resorcin (PAR) mit pD 5,1, 1-(2-Pyridylazo)-2,3-Dihydroxynaphtalin-6-Sulfonsäure mit pD 5,3 und 4-(2-Pyridylazo)orcin mit pD 6,2 trotz erwartenen sterischen Einfluss der Methylgruppe in der Nachbarkeit der Azogruppe. Die Selektivität dieser Reaktionen ist aber klein. Thiazolylazofarbstoffe [4-(2-Thiazolylazo) resorcin, 2-(2-Thiazolylazo) chromotropsäure] sind weniger empfindlich, bei der Thiazolylazochromotropsäure ist pD 4,7 bei pH 5. Für die Reaktionen einiger anderen Azofarbstoffe mit Ti(IV) siehe[10–12]. Von den Hydroxyantrachinonfarbstoffen haben nur die Chinizarinsulfonsäure mit dem Farbumschlag von rotorange nach violett bei pH 5–6 und die Carminsäure mit dem Farbumschlag von orange nach weinrot schon bei pH $\geqslant$ 1 mit einer relativ kleiner Empfindlichkeit, pD 4,7, Bedentung. Andere Derivate dieser Farbstoffgruppe sind nur wenig empfindlich. 1-Hydroxyxanthon reagiert nicht sichtbar.

Die gelben oder gelborangen äthanolischen Lösungen der 2,3,7-Trihydroxyfluorone mit verschiedenen 9-Substituenten färben sich in Gegenwart von Ti(IV) rotviolett (9-Phenylderivat, siehe auch[13]) oder rot (9-Methylderivat) bei pH 5. Die Empfindlichkeit, pD 5,4 bei pH 5.

Empfindlich aber nicht selektiv ist die Reaktion von Resoflavin (Sch. Tab. 771). In schwach sauren Lösungen entstehen rotbraune Färbungen und Niederschlag mit pD 6,0 bei pH 6 (die Reagenslösung in Äthanol ist gelb).

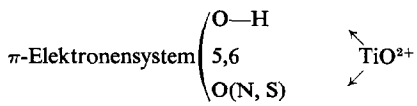
Die positive Reaktion von Ti(IV) wird nicht gehemmt, wenn eine der Ti—O-Bindungen mit einer Ti—N oder Ti—S Bindung im Chelat ersetzt wird. Die übrige Ti—O-Bindung geht dabei zum phenolischen Hydroxyl, selten Carboxyl. Infolge kleinerer Stabilität der Ti—N und Ti–S Bindungen sind auch die Empfindlichkeiten der

Reaktionen mit Ti(IV) geringer. Es bilden sich gelbe bis orange Färbungen oder Niederschläge bei pH 5 mit o-Aminophenol, 8-Hydroxychinolin, 8-Hydroxychinolin-5-Sulfonsäure, 5,7-Dibrom-8-Hydroxychinolin, 8-Hydroxychinaldin, Anthranilsäure, Salicylaldoxim. Eine braunrote Färbung oder Niederschlag entsteht mit 2-Thiopyrogallol bei pH 5,2, eine rosaorange Färbung mit 3-Mercapto-4-Hydroxytoluol.[14,15] Gelbe Färbungen geben auch 3-Hydroxytriazene (3-Hydroxy-1,3-Diphenyltriazen[16]). Einen anomalen Verlauf, wahrscheinlich mit einem Redoxcharakter verbunden, hat die Reaktion von Benzoinoxim mit Ti(IV). In ammoniakalischem Medium entwickelt sich eine violette oder rotviolette Färbung und Niederschlag.

Einwertige Phenolen ebenso wie Verbindungen mit einer  Gruppe

reagieren in wässrigen Lösungen nicht mit Ti(IV).

Auf Grund vorherstehenden Resultate kann man die folgende schematische universelle analytische Gruppe für Titan(IV) ableiten:



Alle analytische Gruppen (I–IX) und daher auch die schematische universelle Gruppe sind nur wenig selektiv für Ti(IV), sie können ebenso als analytische Gruppen für Fe^{3+}, V(IV), UO_2^{2+}, Mo(IV), Nb(V), Ta(V), Sb(III), Ge(IV) betrachtet werden. Deshalb gibt es auch kein absolut selektives Reagens für Ti(IV). Zur Erhöhung der Selektivität der Ti(IV)-Reaktion führt nur die erhöhte Stabilität der Ti(IV)-Chelate mit einigen Reagentien dieser Gruppen, die die Ausführung der Ti(IV)-Reaktion in relativ saurem Medium ermöglicht, und die selektive Reduktion einiger störenden Ionen. Die Selektivität der analytischen Gruppen für Ti(IV) wird praktisch vollkommen aufgehoben, wenn sie an das Farbstoffresonanzsystem angekoppelt sind.

Deshalb wurden die Reaktionen analytisch interessanter Reagentien für Ti(IV), die zum Teil schon in der Literatur erwähnt worden, eingehend studiert und die resultate schematisch in der Tabelle I zusammengestellt.

Von den geprüften Reagentien eignen sich für den selektiven und empfindlichen Nachweis von Ti(IV) die 5-Sulfosalicylsäure bei pH 1,6–2,0 und vor allem die Chromotropsäure bei pH 0–1,0, wo der störende Einfluss fremder Ionen klein ist. Fe^{3+}, Cr(IV), Ce(IV), Tl(III), V(V) werden vorher mit Ascorbinsäure reduziert. Die Ausführung eines direkten Ti(IV)-Nachweises mit Chromotropsäure ist schon früher angegeben worden.[4] 4-(2-Pyridylazo) orcin, Eriochromcyanin R, Resoflavin, Arsenazo und auch Quercetin und Rutin sind zwar ausserordentlich empfindlich für Ti(IV), aber schon in saurem Medium wenig selektiv.

Summary—From a consideration of analytical groups of donor atoms in organic analytical reagents and from a critical evaluation of many organic compounds as reagents for titanium^{IV} a universal analytical group for Ti^{IV} may be derived. Since this group is not very selective for Ti^{IV} and many ions interfere, the reactions of 18 useful reagents for Ti^{IV} have been reviewed. It would appear that chromotropic acid is the most selective and is a sufficiently sensitive reagent at pH 0–1, in the presence of excess of reagent. The influence of some ions can be suppressed following their reduction by ascorbic acid.

Résumé—Discutant les principes théoriques concernant groupes analytiques des atoms donoriques dans les réactifs organiques et les résultats de l'evaluation d'un grand nombre des composés organiques comme réactifs sur titane(IV) nous établissons la groupe universelle atomique pour Ti^{IV}. Parceque cette groupe est seulement peu selective et beaucoup d'ions interferent, les réactions des 18 réactifs organiques qui se sont bien confirmés comme réactifs sur Ti^{IV}, sont examinés en détail. Parmi eux l'acide chromotropique est le réactif le plus sélectif et assez sensitif pour Ti^{IV} à pH 0–1 et en presence d'excess du réactif. L'influence des quelques ions a été supprimée après leur reduction avec l'acide ascorbinique.

LITERATUR

[1] A. Okáč u. L. Sommer, *Coll. Czech. Chem. Comm.*, 1957, **22**, 464.
[2] L. Sommer, *Z. analyt. Chem.*, in Druck.
[3] L. Sommer u. Jin Tsin-jao, *Chem., Listy*, 1961, **55**, 574.
[4] L. Sommer, *Z. analyt. Chem.*, in Druck.
[5] A. K. Babko u. L. M. Gordějeva, *Ukr. Chim. Ž.*, 1960, **26**, 762.
[6] A. K. Babko u. A. I. Volkova, *Z. analyt. Chim.*, 1960, **15**, 587.
[7] M. Ziegler u. O. Glemser, *ibid.*, 1957, **157**, 17.
[8] L. Sommer, *ibid.*, 1957, **169**, 36, 42.
[9] M. Ishidate u. Y. Yamane u. T. Tamano, *Japan Analyst*, 1958, **7**, 170.
[10] F. S. Frum u. G. A. Kistanova, *Trudy po chim. i chim. technol.*, 1958, 578.
[11] F. S. Frum u. E. P. Truščina, *Už. zap. Gorkov. univ.*, 1958, 119.
[12] I. M. Korenman, F. S. Frum u. L. V. Ryžkova, *ibid.*, 1958, 113.
[13] H. Sano, *Japan Analyst*, 1958, **7**, 235.
[14] V. M. Dziomko u. A. I. Čerepachin, *Sbor. stat. vsesojuz. zaoč. politech. Inst.*, 1955, No. 9, 65.
[15] V. M. Dziomko u. A. I. Čerepachin, *ibid.*, 1955, No. 11, 37.
[16] J. Kurfürstová, *Diplomarbeit*, Univ. Brno, 1958.
[17] L. Sommer, *Z. analyt. Chem.*, 1958, 163, 412.
[18] N. A. Tananajev u. G. A. Pančenko, *Z. anorg. Chem.*, 1926, **150**, 163.
[19] S. Ja. Šnajderman, *Izv. Kijev. Politech. Inst.*, 1956, **17**, 197.
[20] A. P. Golovina, I. P. Alimarin u. N. F. Stepanov, *Nauč. Dokl. vysš. školy, chim. i. chim. technol.*, 1958, 285.
[21] P. Szarvas u. Z. Jarabin, u. L. Dede, *Magyar Kém. Folyóirat.*, 1957, **63**, 151.
[22] J. H. Yoe, u. A. R. Armstrong, *Science*, 1945, **102**, 207.
[23] J. H. Yoe ul A. R. Armstrong, *Analyt. Chem.*, 1947, **19**, 100.
[24] R. D. Hall u. E. F. Smith, *J. Amer. Chem. Soc.* 1913, **35**, 138.
[25] T. Fenton, *J. Chem. Soc.*, 1908, **93**, 1064.
[26] R. Castagnon, G. Ducléon, *Trav. Soc. Pharm., Montpéllier*, 1949, **9**, 20.
[27] M. Ziegler u. O. Glemser, *Z. analyt. Chem.*, 1953, **139**, 92.
[28] G. Charlot, *Analyt. chim. Acta*, 1947, **1**, 244.
[29] A. T. Kutejnikov, *Zavodskaya Lab.*, 1958, **24**, 1050.
[30] E. J. Nikitina, *Z. analyt. Chim.*, 1959, **14**, 431.

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PRELIMINARY COMMUNICATION

Analytical use of the sorption of metal complexes of 1,10-phenanthroline and related compounds on silica

METAL complexes of 1,10-phenanthroline (2,2′-bipyridyl, *etc*), which are of cationic nature [$Me(Phen)_m^{n+}$] are very well sorbed on silica. Even the complex with tervalent iron, $Fe_2(OH)_2(Phen)_4^{4+}$, is sorbed quantitatively and very readily. The column is filled with silica of the grade normally used for desiccators. From the point of view of the column resistance, the best particle size of the silica was found to be 0·2–0·3 mm. For sorption of microgram amounts of metals in the form of complexes with the complex forming reagents mentioned, a column about 5 cm long is satisfactory. After separation of iron, which is achieved by elution with hydrochloric acid and a suitable buffer solution, the sorption proceeds at a flow rate of about 3 ml per min.

Quantitative sorption of μg–or tenth μg–amounts of the phenanthroline complexes $Fe(Phen)_3^{2+}$ and $Co(Phen)_3^{2+}$ proceeds under the conditions described in the pH range 2–9. These complexes can be desorbed by a 10–20% aqueous alkaline solution of potassium iodide, or by a saturated methanolic solution of the same reagent. This desorption is caused by the formation of neutral ion-association complexes such as [$Fe(Phen)_3^{2+}$, $2I^-$] and [$Co(Phen)_3^{2+}$, $2I^-$], which were originally used for the extraction of phenanthroline complexes with chloroform.[1,2] Reasoning from these results, it may be deduced that other complexes of this type might also be desorbed from the silica column.

The selectivity of the colorimetric determination of traces of iron as ferroïn could be increased, using EDTA[1] or citric acid[3] at a suitable pH to mask other metals, which might interfere in the determination, especially at high metal concentration. The complexes of many metals with EDTA or citric acid are not sorbed on silica over a wide pH range, because they are anionic. This phenomenon could be used for the selective separation of traces of iron from other metals, the iron being sorbed as ferroïn and, after desorption with potassium iodide, determined colorimetrically.

This procedure is suitable for the determination of traces of iron in the presence of coloured ions; we were easily able to determine 10^{-4}% of iron in nickel and chromium.

At present we are studying the sorption of other phenanthroline and bipyridyl complexes, and of the complexes with other suitable reagents which form cationic complexes (e.g. with pyridine or ammonia). This work is directed to the elaboration of analytical procedures for selective determinations of traces of metals. Detailed results will be published shortly.

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Summary—The sorption of iron—1,10-phenanthroline and similar cationic complexes on silica may be used to increase the sensitivity of the colorimetric determination of traces of the metal.

Zusammenfassung—Die Sorption von Eisen-1,10-Phenanthrolin und ähnlicher Kationenkomplexe kann ausgenutzt werden um die Empfindlichkeit der kolorimetrischen Bestimmung von Spurenmetallen zu erhöhen.

Résumé—L'adsorption sur silice de la 1,10-phénanthroline de fer et des complexes cationiques semblables peut être utilisée pour augmenter la sensibilité du dosage colorimétriques de traces du métal.

REFERENCES

[1] F. Vydra and R. Přibil, *Talanta*, 1959, **3**, 72.
[2] F. Vydra, M. Kopanica and R. Přibil, *Chem. listy*, 1960, **54**, 1036.
[3] J. O. Hibbits, W. F. Davis and M. R. Menke, *Talanta*, 1961, **8**, 163.

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SHORT COMMUNICATIONS

An investigation of the determination of titanium by flame photometry

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VARIOUS methods have been used for the determination of titanium in metal alloys and other materials[1] but there is no record of the use of flame photometry for the determination of this element.

When heated in an oxygen/fuel flame, titanium emits a series of overlapping oxide bands with band heads at 497, 518 and 715 mμ.[2,3] These bands are of low intensity, but the possibility of using these emissions for quantitative analysis has now been investigated.

Flame photometry of titanium solutions

The intensity of emission at 518 mμ of a series of standard titanium solutions was measured with a Hilger H 700 Uvispek Spectrophotometer fitted with a Flame-Photometer Attachment. Solutions containing 200, 400, 1000 or 2000 ppm of Ti were used as the check standards in these measurements, and it was found that the relationship between intensity of emission and amount of titanium present was linear using the 200-ppm Ti check standard. With higher concentrations of titanium in the test solutions and check standard, the calibration curves became convex in shape.

Accordingly, for flame photometric studies, it is desirable, but not essential, to use a standard check solution containing 200 ppm of Ti, and unknown test solutions of lower concentration. Under these conditions, a precision in emission readings (expressed as standard deviation) of $\pm 3{\cdot}5\%$, which corresponds to ± 7 ppm of Ti, was obtained. By comparison, the precision obtained in emission values using a 1000-ppm Ti solution as check standard was $\pm 4{\cdot}1\%$, which corresponds to ± 41 ppm of Ti.

Interferences

An interference study showed that most of the metals which accompany titanium in a hydrous oxide analytical group separation interfere with the flame-photometric determination of titanium.

The presence of zirconium and phosphorus had little significant effect on the intensity of emission of a standard titanium solution, but the following elements enhanced the emission at 518 mμ, the magnitude of the interference effect decreasing in the order shown: Cr > Al > Mo > V > Fe > Mg > Na.

This list was not extended further, since the marked intensity of these interfering emissions demonstrated quite clearly that flame photometry for titanium could only be applied to solutions which were virtually free of other cations. The determination of titanium in alloys, *etc.* by flame photometry thus requires an efficient preliminary separation of titanium from most other elements.

The separation of titanium from interferants

Since speed and simplicity are important attributes of flame photometric methods of analysis, the separation procedure used to isolate titanium should also possess these attributes.

A variety of methods of separation have been proposed[1] but few satisfy the requirement of speed. A method which is reasonably fast is that used by Pickering[4,5] as a preliminary step in the colorimetric determination of titanium in iron ores and alloy steels, but the method has the disadvantage that the reproducibility of the separation is of the order of $\pm 3{\cdot}5\%$. For use in flame photometric determinations, it is also necessary to reduce the concentration of impurities in the product initially isolated by reprecipitation, and then to compensate for remaining traces of impurity by using a standard addition technique for the preparation of the check standard.

A series of tests were made using this separation technique as a preliminary step in the determination of titanium in a sample of ferro-titanium (35% Ti) and in a sample of titanium-aluminium alloy (70% Ti). When a differential absorptiometric method similar to that proposed by Milner and Phennah[6] was used as the means of determining the titanium content, the results obtained had a reproducibility of $\pm 3{\cdot}5\%$. This colorimetric method is known for the high precision obtainable and hence this variation merely reflects the inefficiency of the separation technique. Using the flame

photometric technique for the determination of the titanium, the results had a reproducibility of ±4%. This slight increase in error is to be expected from the poor precision observed in readings on pure titanium solutions (±3·5%).

Thus, although other methods of separation may eliminate the error introduced by this particular separation technique, the limitations inherent in flame photometric determinations still leave such methods at a disadvantage if suitable alternate colorimetric methods are available.

DISCUSSION

The investigations have shown that it is possible to determine titanium by flame photometry, although limitations inherent in the technique militate against many practical applications. Probably the most restrictive limitation is the need to isolate titanium in a pure form before atomisation in the flame. Most methods for titanium do require a preliminary separation from interferants but rarely is it necessary to ensure such complete removal of interferants as in the flame method.

A second major limitation is the current existence of colorimetric techniques which are comparable in speed to flame photometric determinations but which are far more accurate and reproducible.

Acknowledgment—Two of us (C. L. C. and W. F. P.) wish to thank the Queen's University of Belfast for the research fellowships which enabled us to undertake this research. One of us (W. F. P.) also wishes to thank the University of New South Wales for a grant of study leave.

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Summary—An investigation has been made of the determination of titanium by flame photometry.

Zusammenfassung—Eine Methode zur flammphotometrischen Bestimmung von Titan in Letierungen wurde entwickelt.

Résumé—Les auteurs ont mis au point une méthode de dosage du titane dans les alliages par photométrie de flamme.

REFERENCES

[1] W. T. Elwell and D. F. Wood, *Metal Ind. (London)*, 1960, **97**, 23, 51, 67.
[2] M. Whisman and B. H. Eccleston, *Analyt. Chem.*, 1955, **27**, 1861.
[3] F. Burriel-Marti and J. Ramirez-Munoz, *Flame Photometry*, Elsevier Publishing Co., London, 1957, p. 167.
[4] W. F. Pickering, *Analyt. Chim. Acta*, 1953, **9**, 324.
[5] *Idem, ibid.*, 1955, **12**, 572.
[6] G. W. C. Milner and P. J. Phennah, *Analyst*, 1954, **79**, 414.

The determination of nitrite ion in the presence of large quantities of azide ion

(*Received* 6 *January* 1962. *Accepted* 23 *January* 1962)

INTRODUCTION

THE detection and determination of very small quantities of nitrite ion in azides has appeared to be a difficult problem because of the lack of sensitivity of X-ray procedures and because the two ions interact in aqueous solutions. Titration procedures for the quantitative determination of azides with nitrite salts[1] and nitrous acid[2] have been reported.

This note describes a spectrophotometric procedure in which traces of nitrite ion are quantitatively determined in potassium azide crystals by the use of n(1-naphthyl)-ethylenediamine dihydrochloride and sulphanilic acid reagent.

EXPERIMENTAL

Reagents

N-(1-naphthyl)-ethylenediamine dihydrochloride and sulphanilic acid reagent: Dissolve 2·5 g of sulphanilic acid in 400 ml of an aqueous solution containing 20 ml of glacial acetic acid, then add with a pipette 10 ml of 0·1% aqueous *N*-(1-naphthyl)-ethylenediamine dihydrochloride and dilute to the mark with water in a 500-ml volumetric flask.

photometric technique for the determination of the titanium, the results had a reproducibility of ±4%. This slight increase in error is to be expected from the poor precision observed in readings on pure titanium solutions (±3·5%).

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REFERENCES

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[2] M. Whisman and B. H. Eccleston, *Analyt. Chem.*, 1955, **27**, 1861.
[3] F. Burriel-Marti and J. Ramirez-Munoz, *Flame Photometry*, Elsevier Publishing Co., London, 1957, p. 167.
[4] W. F. Pickering, *Analyt. Chim. Acta*, 1953, **9**, 324.
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Silver sulphate solution: Use only the clear supernatant solution or filtrate from a saturated solution.

Standard nitrite solution: Prepare a stock solution containing 0·4970 g of sodium nitrite per litre. Dilute 100 ml to 1 litre. Dilute 50 ml of this second solution to 1 litre (1 ml = 0·0005 mg of nitrogen or 0·001642 mg of nitrite ion).

Potassium or sodium azide solution: Prepare an aqueous solution containing 5·0 mg of azide per ml.

Water: Distilled water free from nitrites, nitrates, and oxides of nitrogen.

Apparatus

Beckman Model B spectrophotometer with 2-cm corex cells.

Proposed procedure

Calibration curve: Pipette 25 ml of the saturated silver sulphate solution and then 10 ml (50 mg) of the standard azide solution into each of a series of 50-ml volumetric flasks. Pipette into each flask the required amount of standard nitrite solution to give a range from 0·5 to 5·0 μg of nitrogen per 50 ml, using one flask as the reagent blank. Dilute each solution to the mark, mix, allow to stand 5 min for complete precipitation, then filter and collect the filtrate in a small dry beaker. Use a dry funnel and dry close-textured filter paper to avoid dilution errors and possible contamination from any very fine silver azide precipitate. Discard the first 5–10 ml of the filtrate. Pipette 15 ml of each solution into the corresponding 25-ml volumetric flask, then add 10·0 ml of the reagent solution to each flask, including the blank. After mixing, allow 20 to 30 min for colour development. Take absorbancy readings at 550 mμ using 2-cm cells. The system conforms to Beer's law.

Unknowns: The samples should not contain more than 50 mg of the azide ion for effective precipitation by 25 ml of the saturated silver sulphate solution. Transfer the weighed sample to a 50-ml volumetric flask containing 25 ml of the saturated silver sulphate solution. Dissolve the sample, dilute to the mark, mix, and allow to stand 5 min for complete precipitation. Continue as directed for the calibration curve. From the calibration curve determine the nitrogen in the sample.

Weight of nitrogen $\times$ 3·2844 = Weight of nitrite ion.

DISCUSSION

Radiated potassium azide crystals developed a brownish colour, more intense at the point of radiation impact. Electron paramagnetic resonance studies suggested the presence of oxygen, but X-ray analytical procedures were too insensitive to indicate the material present.

When small quantities of the contaminated potassium azide crystals were dissolved in the reagent, the "fleeting" reddish-purple colour suggested the presence of the nitrite ion before it was destroyed by the azide ion. When a few ml of the nitrite-reagent complex solution were added to a 0·1*M* concentration of azide ion the colour was destroyed almost immediately. This suggested that if the concentration of the azide ion could be reduced to a low level, such as the concentration of azide ion in equilibrium with silver azide (solubility $5{\cdot}6 \times 10^{-5}$ mole/1.[3]), then the reaction rate between the low concentrations of the azide ion and the free nitrite ion from the nitrite-reagent complex would be very low, and a reasonably stable colour would be possible. Therefore, a small quantity of dry sodium azide and sodium nitrite in the approximate ratio of 50 to 1 by weight was placed in a dry test tube, then dissolved with excess saturated silver sulphate solution (solubility $2{\cdot}68 \times 10^{-2}$ mole/1.[4]). The silver azide was filtered and the reagent added to the filtrate. A stable colour developed. No colour developed when the reagent was added to an equal volume of saturated silver sulphate solution. Twenty min were necessary for complete colour development (Table 1).

TABLE I. TIME REQUIRED FOR COLOUR DEVELOPMENT

Nitrogen as nitrite ion, μg		Time, *min*
Taken	Found	
5·00	3·10	5
5·00	4·09	10
5·00	4·68	15
5·00	5·00	20
5·00	5·00	25
5·00	5·00	35

In a series of five 5-μg samples of nitrogen as the nitrite ion in the presence of 50 mg of azide ion an average of 4·99 μg of nitrogen was found with a standard deviation of 0·012.

The effect of leaving the solution in contact with the silver azide precipitate longer than the initial 5 min allowed for complete precipitation is indicated in Table II.

TABLE II. EFFECT OF ALLOWING SOLUTION TO REMAIN IN CONTACT WITH SILVER AZIDE

Time* after mixing, *min*	Azide ion, *mg*	Nitrogen as nitrite ion, μg	
		Taken	Found
10	50	5·00	4·96
25	50	5·00	4·85
40	50	5·00	4·72
55	50	5·00	4·64
70	50	5·00	4·58
130	50	5·00	4·53

* Time in addition to the 5 min allowed for complete precipitation.

The use of solid silver sulphate in place of the saturated solution to precipitate the silver azide from the dissolving azide-nitrite mixture yielded very low results. The rate of solution of the dry silver sulphate mixed with the azide-nitrite salts is not sufficiently great to prevent appreciable reaction of the azide with the nitrite present.

Very low results were obtained when the complexing agent was added to the solution without filtering the silver azide. The low results are probably caused by the acetic acid in the complexing reagent solution reacting with the silver azide to liberate hydrazoic acid, which in turn reacts with the nitrite ion. For this reason a close-textured filter paper should be used to filter the silver azide to ensure a contamination-free solution with respect to silver azide.

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Summary—The azide ion reacts with the nitrite ion when in solution. In order to determine the nitrite ion quantitatively in the presence of azides, the azide ion is immediately precipitated by dissolving the salt(s) in a saturated solution of silver sulphate, then filtered. A fraction of the filtrate treated with *N*-(1-naphthyl)-ethylenediamine dihydrochloride and sulphanilic acid reagent produces a stable colour and is the basis for the spectrophotometric procedure.

Zusammenfassung—Um Nitrition neben Azidion quantitative zu bestimmen wird die Probe in gesättigter Silbersulfatlösung gelöst. Das hierbei gefällte Silberazid wird abfiltriert. Ein Teil des Filtrates wird mit *N*-(1-Naphthyl)-äthylen-diamindihydrochlorid und Sulfanilsäure behandelt. Die entwickelte Färbung wird photometrisch ausgewertet.

Résumé—L'ion azide réagit avec l'ion nitrite en solution. Afin de doser quantitativement l'ion nitrite en présence d'azides l'ion azide était précipité par dissolution du (ou des) sels dans une solution saturée de sulfate d'argent, puis filtré. Une fraction du filtrat traité par le chlorhydrate de n(naphtyl-1) éthylénediamine et le réactif acide sulfanilique produisait une coloration stable et était la base d'une méthode spectrophotométrique.

REFERENCES

[1] H. F. Reith, Dissertation, Utrecht, 1929; I. M. Kolthoff and R. Belcher, *Volumetric Analysis*, Vol. III. Interscience Publishers, Inc., New York, 1957, p. 661.
[2] J. F. Reith and J. H. A. Bouwman, *Pharm. Weekblad*, 1930, **67**, 475.
[3] E. H. Riesenfeld and F. Muller, *Z. Electrochem.*, 1935, **41**, 87.
[4] Atherton Seidell and William F. Linke, *Solubilities of Inorganic and Organic Compounds*. D. Van Nostrand Co., Inc., New York, 1952, p. 22.

Semimicro iodometric determination of thallium^{III} by an amperometric method with two polarisable electrodes

(*Received* 15 *January* 1962. *Accepted* 29 *January* 1962)

THE iodometric determination of thallium^{III} has been described by several workers using starch indicator[1,2] as well as by a potentiometric method.[3] It has been stated that the colour of the starch-iodine complex is somewhat obscured by a muddy greenish-brown precipitate of thallium^{I} iodide and the adsorption of iodine by thallium^{I} iodide prevents attainment of equilibrium.[1] Photodecomposition[1] of thallium^{I} iodide also gives rise to incorrect results if proper care is not taken. In view of these difficulties an attempt has been made to study the amperometric determination of thallium^{III} using a system of two polarisable electrodes and it has been observed that very accurate results can be obtained even at concentrations down to $10^{-4}N$ and the disadvantages of visual indicators are completely eliminated.

Standard 0·01*N* thallium^{III} solution was prepared by dissolving 2·2839 g of thallium^{III} oxide (Specpure) in hot concentrated sulphuric acid and diluting to 1 litre; sufficient dilute sulphuric acid must be added to prevent the precipitation of thallium^{III} oxide and to give a final acid concentration of 0·5–1·0*N*. A 0·01*N* solution of sodium thiosulphate was standardised against potassium dichromate. Before carrying out a titration an aliquot of thallium^{III} solution was pre-oxidised with bromine[1] to ensure that all of the thallium was present in the tervalent state. Iodine was then liberated from the thallium^{III} solution by adding 0·5 g of potassium iodide and the titration vessel was placed in a cardboard or wooden box to prevent direct light falling on it. The electrode system consisted of two

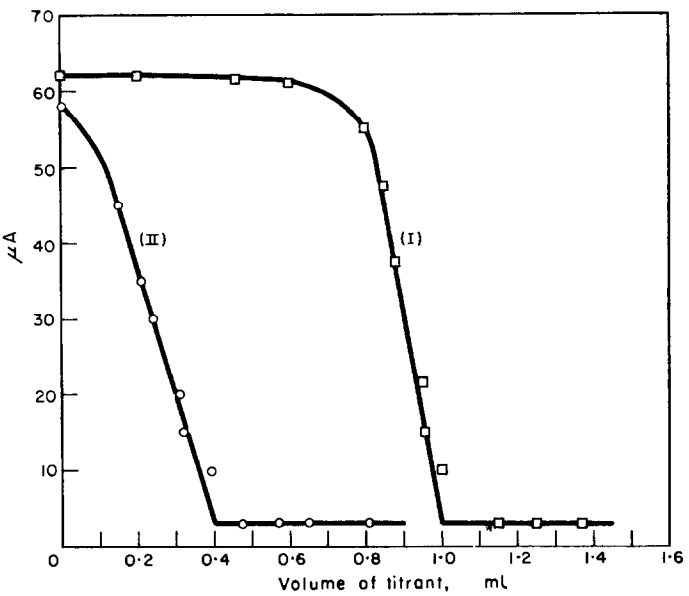


FIG. 1.—Amperometric titration curve of thallium^{III}:
I—0·01*N* solution,
II—$10^{-4}N$ solution.

similar platinum electrodes across which a small e.m.f. (20–30 mV) was applied and the current was measured by a multirange micro-ammeter. (E. H. Sargent's 'Ampot' Electrometric Titration Apparatus was found to be very satisfactory for this purpose). Fig. 1 shows titration curves corresponding to 0·01*N* and $10^{-4}N$ thallium^{III} solutions, respectively, and the results of some of the determinations are given in Table I.

In solutions containing higher concentrations (0·01*N*) of thallium^{III} the system is well poised because of the presence of the iodide-tri-iodide couple and the current maintained a constant value (50–70 mA). When the concentration of iodine was decreased considerably the current became diffusion controlled, being proportional to the concentration of iodine. After the end-point the

TABLE 1.

Initial concentration of titrant, *mM*	Amount of Tl^{III}, *mg*		Error, %
	Taken	Found	
10·0	40·88	40·90	0·30
5·0	20·44	20·42	−0·02
2·5	10·22	10·27	0·50
1·0	4·09	4·07	−0·50
0·5	2·044	2·065	1·00
0·2	0·817	0·823	0·74

Volume of titration mixture = 20 ml

current reduced to nearly zero. In more dilute solutions ($10^{-4}N$) the end-point is best determined by extrapolation, but up to a concentration of $0{\cdot}01N$ the dead-stop end-point method can be followed. The method can be extended to the determination of thallium in industrial preparations after extraction[4] of thallium trichloride with ether.

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Summary—An iodometric method for the semimicro determination of thallium^{III} is described, the end-point being determined amperometrically using two polarisable electrodes. The advantages of the amperometric method over the visual indicator method are discussed.

Zusammenfassung—Eine jodometrische Methode zur Halbmikrobestimmung von Thallium(III) wurde beschrieben, wobei der Endpukt amperometrisch mit zwei polarisierbaren Elektroden bestimmt wird. Die Vorteile der amperometrischen Methode gegenüber visueller Indication werden dargelegt.

Résumé—Les auteurs décrivent une méthode iodométrique de semi-microdosage du Thallium(III), dans laquelle le point équivalent est déterminé par ampérométrie en utilisant deux électrodes polarisables. Les avantages de la méthode ampérométrique sur la méthode visuelle sont donnés.

REFERENCES

[1] C. W. Sill and H. E. Peterson, *Analyt. Chem.*, 1949, **21**, 1208.
[2] W. Langer and A. Govel, *Z. Erzbetghan V. Metallhuttenn*, 1950, **3**, 370.
[3] W. R. A. Hollens and J. F. Spencer, *Analyst*, 1935, **60**, 673 .
[4] A. A. Noyes, W. L. Bray and E. B. Spear, *J. Amer. Chem. Soc.*, 1908, **30**, 515.

The effect of some anions on the spectrophotometric absorption of bis-(di-n-octylethylenediamine)-Cu^{II} complexes in hexone.

(*Received* 19 *January* 1962. *Accepted* 29 *January* 1962)

IN the course of investigating the extraction of ion-association complexes of various metal chelates of *N*-alkyl substituted ethylenediamines, we observed an interesting phenomenon with the Cu^{II} chelate of di-n-octylethylenediamine. The reagent was made by following Linsker and Evans' procedure[1] for the preparation of mono-n-octylethylenediamine, in which octyl bromide reacts with excess of anhydrous ethylenediamine. The product, when recrystallised from ether, had a melting point of 58°, and was shown to be the di-n-octyl, rather than the mono-n-octyl derivative, by elemental analysis and equivalent weight determinations. The position of the octyl groups could not be ascertained definitely, but the compound is probably the symmetrically substituted *N,N'*-di-n-octylethylenediamine.

We noted that the compound extracted copper from sulphate solutions into isobutylmethylketone, and that the separation was improved by the addition of sodium chloride. It was also noted that the

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REFERENCES

[1] C. W. Sill and H. E. Peterson, *Analyt. Chem.*, 1949, **21**, 1208.
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We noted that the compound extracted copper from sulphate solutions into isobutylmethylketone, and that the separation was improved by the addition of sodium chloride. It was also noted that the

colour of the extract changed when sodium chloride was added, that this new colour could be changed by shaking with sodium bromide, and that the bromide colour could in turn be displaced by sodium iodide, if care were taken to avoid the release of iodine.

The absorption maxima and molecular absorbtivities of the copper extract in the presence of various sodium salts were measured;

The values are given in Table I.

TABLE I. EFFECT OF ANIONS

X	λ_{max}	ε
Chloride	700	775
Bromide	690	282
Acetate	665	137
Bicarbonate	665	
Sulphate	660	
Thiosulphate	650	248
Nitrate	590	130

The measurements were made on solutions prepared by extracting 5 ml of 10^{-2} *M* copper solution with 5 ml of 2×10^{-2} *M* amine solution in iso-butylmethylketone in the presence of a large excess of the sodium salt of the anion in question. Wherever possible the copper salt used to prepare the copper^{II} solution was that containing the same anion.

An estimate of the ease of displacement of an anion from the complex was made by starting with one complex, adding increasing amounts of the sodium salt of another anion and determining the wavelength of maximum absorption of the resulting mixture; the absorption bands were too broad to follow the decrease in absorption at one wave-length and the increase at another. The result for chloride and nitrate is shown in Fig. 1. Assuming a reaction such as

$$(\text{di-Octen})_2CuX_2 + 2NaX' \rightleftharpoons (\text{Di-Octen})_2CuX_2' + 2NaX,$$

it is noted that nitrate displaces the chloride from the complex more readily than *vice versa*.

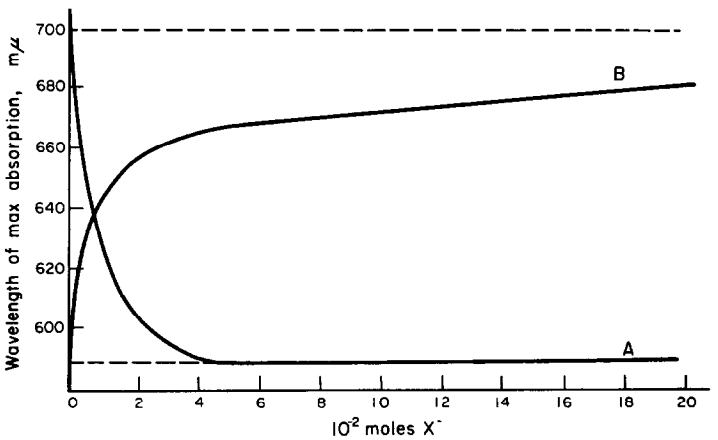


FIG. 1.—Anion replacement in Cu^{II} Di(di-n-octylethylenediamine) ion-association complex in iso-butylmethylketone

(A) Cu^{II} (di-octen)$_3$Cl$_2$ with nitrate addition.

(B) Cu^{II} (di-octen)$_2$(NO$_3$)$_2$ with chloride addition.

Reagent solutions contain $2{\cdot}5 \times 10^{-5}$ Mole of Cu(NO$_3$)$_2$ [or CuCl$_2$] $8{\cdot}5 \times 10^{-5}$ Mole. Di-octen in hexone medium.

Because of the pressure of circumstances we have been unable to investigate the phenomenon as fully as it deserves, but hope to make further investigations in the future.

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Summary—A brief description is given of the effect of halide anions, etc. on the optical characteristics of bis (di-n-octyl ethylenediamine)-Cu^{II} extracted from an aqueous phase into iso-butylmethylketone.

Zusammenfassung—Eine kurze Beschreibung des Effektes von Halidionen usw. auf die optische Charakteristik von Bis (di-n-octyl äthylendiamin) Cu(II) (aus wässriger Lösung in Butylmethylketon extrahiert) wird gegeben.

Résumé—Les auteurs décrivent brièvement l'action des anions halogénures. . . sur les caractéristiques optiques du bis(di-n-octyléthylène diamine) Cu(II) extrait par l'isobutylméthylcétone à partir d'une solution aqueuse.

REFERENCE

[1] F. Linsker and R. L. Evans, *J. Amer. Chem. Soc.*, 1945 **67**, 1581.

Talanta, 1962, Vol. 9, pp. 459 to 467. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEWS

The Encyclopedia of Spectroscopy. Edited by GEORGE L. CLARKE. Reinhold Publishing Corpn., New York, 1960. Pp. xvi + 787. 200/-.

THIS weighty but handsome volume claims, with some justification, to present an authoritative survey of the entire field of spectroscopy including lengthy sections on absorption, emission, flame, infrared, mass and X-ray spectroscopy, each section comprising several articles. Shorter sections deal with band, β-ray, electron paramagnetic resonance, fluorescence, phosphorence, γ-ray, micro-wave, neutron, Raman and solar spectrometry. The 160 articles, with the exception of about two, were written by American authors, and this has introduced a noticeable bias, particularly in descriptions of available instruments and techniques. Furthermore, the late Mr. F. Twyman, F.R.S., would doubtless have accepted in his customary philosophical manner the statement that "The development of spectroscopy in its application to chemical analysis may be traced from an experimental programme of the National Bureau of Standards, first reported in 1922" (p. 113)! Although the dust cover states that each article was especially written for inclusion in this volume, the text indicates that twenty of them were taken from other sources.

Many of the articles are excellently prepared and presented, but some are ephemeral or polemical in nature and somewhat out of place in a volume that claims to be a reference book. However, the standard of presentation is regrettably by no means uniform and a few examples may be quoted to indicate the carelessness of some statements: (1) "Spectral regions absorbing more than others are known as absorption bands" (p. 1). (2) "Accordingly, wandering of the arc off axis caused large changes in the intensity of the slit" (p. 102). (3) "To return to their normal orbits, the electrons must release the energy with which they have been charged. They return from the excited state to the ground state in definite steps, releasing energy stepwise in the form of light. Each step accounts for the presence of a specific frequency of light and hence the presence of a spectral line on the photographic plate" (p. 108). (4) "The measured transmission of the line therefore is in direct proportion to the amount of element in the sample" (p. 111).

The main criticism of this volume must be that the intention to provide an encyclopedia for reference purposes has not been fulfilled because there is almost a complete absence of cross-references. The shorter sections, such as that on flame photometry, can be studied and assimilated reasonably readily, but the longer ones, covering 200–300 pages, are not in a form suitable for those seeking immediate information. For example, in the article dealing with isotope ratio determination, reference is made to the Fabry-Perot interferometer (p. 210) but there is no indication that a fuller description of the instrument is on p. 258, rather unexpectedly in an article entitled *Optical qualities of spectroscopic instruments*. Similarly, the article on hollow-cathode discharge tubes (p. 200) makes no reference to their use in atomic absorption spectroscopy (p. 12). Although there are separate articles on the analysis of molybdenum, silicon-germanium alloys and tungsten, anyone seeking information on the analysis of, for instance, steels or copper alloys by emission spectroscopy would have difficulty in finding it; doubtless all the information is there but not in a form for easy reference. Similarly, the article on determination of detonation temperature reminds the reader of many other applications of spectroscopy to temperature measurement, but he is left without guidance as to where to find them. In fact, the only reason for calling the volume an encyclopedia seems to be that a miscellaneous collection of articles (which do indeed cover their subjects reasonably comprehensively) has been arranged in alphabetical, rather than in logical, order. If a second edition is contemplated, the editor could undertake with advantage the introduction of a full system of cross-references, together with the omission of some repetitive or ephemeral matter. The same objectives could be attained by re-arranging the material in a more formal order, with a comprehensive index.

It will be appreciated that this book cannot be recommended unreservedly to those many people who are interested in one aspect or another of spectroscopy. However, those who can afford the somewhat large price and who have the time to study it at leisure, rather than as a reference book, may derive some profit.

M. MILBOURN

Advances in Fluorine Chemistry. Vol. II. Edited by M. STACEY, J. C. TATLOW and A. G. SHARPE. Butterworths Scientific Publications, London, 1961. 45s.

THIS volume reaches the same excellent standard as its predecessor. Each of the six chapters is a detailed and fully documented survey written by an expert. The literature references cover the period up to 1960, and many references to recent unpublished work are also given. All the authors have produced contributions which can be read with pleasure and interest by non-specialists, as well as being valuable to specialists.

The chapters are: *The Thermochemistry of Organic Fluorine Compounds* by C. R. Patrick; *Fluorine Resources and Fluorine Utilisation* by G. C. Finger; *Mass Spectrometry of Fluorine Compounds* by J. R. Majer; *The Fluorination of Organic Compounds using Elementary Fluorine* by J. M. TEDDER; *The Fluorides of the Actinide Elements* by N. Hodge; *The Physiological Action of Organic Compounds containing Fluorine* by B. C. Saunders.

There is an important subject which has not figured in either volume of this work: the properties and chemical transformations of fluorocarbons and their derivatives. This has now attained the status of a branch of chemistry in itself, yet no recent general account of it seems to be available. The reviewer hopes that it will not be neglected in future volumes of *Advances*.

H. G. HEAL

Chemical Analysis. An advanced text and reference. HERBERT A. LAITINEN. McGraw-Hill Book Company, Inc., New York, Toronto, London, 1960. Pp. xiv + 611, $12.50.

PROFESSOR LAITINEN'S book, published in the McGraw-Hill *Series in Advanced Chemistry* represents an entirely new concept in textbooks of analytical chemistry, both in arrangement and in contents. Only fundamental principles are described, without any laboratory prescriptions. A high standard of physicochemical background is presumed, the book being written for the advanced undergraduate and early graduate level. The book deals with classical analytical chemistry; only a few instrumental methods are mentioned.

The arrangement of the book is very interesting, although sometimes controversial. Following the Preface, and the Introduction (Chapter 1), Chapter 2 deals with the theory of equilibrium and activity. The chapter on acid-base equilibria in water (3) comprises pH, titration curves and indicators. The "theoretical indicator error", introduced following Benedetti-Pichler, could perhaps be replaced or at least supplemented by Kolthoff's "indicator error", which has a greater importance from view of analytical practice. The next chapter (4) deals with non-aqueous solutions, and is based theoretically on the Brønsted theory: proton-free solvents are not treated. In Chapter 5, applications of acid-base titrations are outlined in principle; mostly those methods which are of interest because of their theoretical backgrounds are treated, among which, perhaps, titration of boric acid might also have been included. The five following chapters (6–10) deal with solubility, and the formation and properties of precipitates. The quantitative discussion of the dependence of solubility on particle size is very interesting, and is a new topic in analytical textbooks. Nucleation, crystal growth, ageing, and precipitation from homogeneous solutions are treated from the standpoint of the most recent investigations. Chapter 11 deals with thermal decomposition and volatilisation, and includes thermogravimetric analysis. Precipitation titrations (Chapter 12) are treated relatively briefly, and in Chapter 13 complex-forming titrations are detailed; first of all, those using EDTA. Among indication methods the mercury electrode is mentioned in addition to visual indicators; here perhaps, however, Xylenol Orange might also have been treated.

The next chapter (14), dealing with organic reagents and extraction methods, is perhaps a little bit heterogeneous in character; extraction methods are also discussed later in Chapter 25. The theoretical Chapter 15, concerned with electrode potentials, contains a valuable quantitative treatment of the effect of complex-forming agents. Electrolytic separations and electroanalysis (Chapter 16) includes also controlled-potential electrolysis and coulometric titrations. The next seven chapters (17–23) deal with redox titrations; in particular, cerimetry (20) and methods involving iodine (21) are discussed thoroughly. The theory and applications of the Karl Fischer titration are also outlined here. Chapter 24, on reaction rates in chemical analysis includes also catalytic and induced reactions. Chapter 25, on multistage separation methods, involving distillation, extraction, chromatography (gas, liquid, paper) and ion-exchange, is detailed in its treatment of these topics. The next chapter (26) deals with statistics in quantitative analysis. This part of the book is arranged and written especially well, giving adequate (but not too much) detail for an analytical chemist. The placing of Chapter 27 last, dealing as it does with problems of sampling, might be criticised, although the author justifies this arrangement by the need for a basis of mathematical statistics for a quantitative treatment. A subject index completes the book.

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A. D. CAMPBELL

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discussion of the occurrence of the element, industrial processes, toxicology, a description of the important physical and chemical properties of the element, sampling procedures, separation and isolation techniques, qualitative and quantitative analyses, discussion of selected methods for the determination of the element, and a few detailed laboratory procedures.

Despite the organisational uniformity, some of the authors have succeeded in personalising their treatment, which leads to some rather unusual presentations. For example, F. S. Grimaldi, whose interest in the solvent extraction of uranium and thorium is well known, devotes as much space to the extraction of thorium with tributyl phosphate as he does to gravimetric methods for the separation and determination of this element.

It is difficult to understand why reference is not made to the monograph **Analytical Chemistry of Titanium Metals and Compounds**, by Maurice Codell (also edited by P. J. Elving and I. M. Kolthoff). Surely, considering the brevity of the treatment here, the reader should be referred to the only book devoted entirely to the analysis and determination of titanium. Furthermore, no reference is made to the work of J. C. White on the extraction and determination of the titanium thiocyanate complex with tri-*n*-octyl phosphine oxide, the most nearly specific and sensitive method for titanium known to this reviewer. Finally, no reference is made to the inert gas fusion method for determining oxygen in titanium metal, a peculiar omission because of the fact that it was the application of this technique by the ASTM task force which "sold" the Leco oxygen analyser to the analyst.

It is unfortunate that the statement "there is no method known in which a quantitative separation of zirconium and hafnium can be obtained" was made so shortly before successful ion-exchange separations were performed by the U.S. Bureau of Standards and (independently of course) by the Russians. In Table IX, p. 92, it is stated that zirconium can be precipitated with *m*-nitrobenzoic acid and separated from thorium, in contradiction to the literature cited. A minor omission is the fact that Duval has reported that the zirconium oxide obtained when some compounds are ignited may be oxygen deficient.

Although I was dissatisfied with the meagre treatment given to the Kjeldahl determination and to the Nesslerization reaction, I was impressed by the wealth of information presented in the chapter on nitrogen. I must admit that I was unaware of a great deal of the material presented.

The material on phosphorus is presented in a scholarly manner and contains much of interest to the practicing analyst. In common with other writers on phosphorus, the authors state that appreciable loss of orthophosphoric acid occurs when boiling a solution of this substance in sulphuric acid. This could easily mislead those engaged in trace determinations, inasmuch as little, if any, loss of phosphorus occurs when 1-mg amounts are heated in the presence of fuming sulphuric acid for a reasonable length of time.

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J. O. Hibbits

Pharmaceutical Analysis. Edited by Takeru Higuchi and Einar Brochmann-Hanssen. Interscience Publishers, New York 1961. Pp. 854, $28.50

This compilation attempts to cover much of the expansive field of pharmaceutical analysis. The methods and procedures, drawn entirely from the literature, are organised under chapter headings which include related or similar chemical structures on one hand and pharmacologically similar compounds of dissimilar or unrelated structure on the other.

The introductory chapter, orienting pharmaceutical analysis and its development against the background of the Federal Food, Drug and Cosmetic Act, along with a good description of the special problems of the pharmaceutical industry arising from the interpretations of the Act and regulations promulgated under it, is excellent.

discussion of the occurrence of the element, industrial processes, toxicology, a description of the important physical and chemical properties of the element, sampling procedures, separation and isolation techniques, qualitative and quantitative analyses, discussion of selected methods for the determination of the element, and a few detailed laboratory procedures.

Despite the organisational uniformity, some of the authors have succeeded in personalising their treatment, which leads to some rather unusual presentations. For example, F. S. Grimaldi, whose interest in the solvent extraction of uranium and thorium is well known, devotes as much space to the extraction of thorium with tributyl phosphate as he does to gravimetric methods for the separation and determination of this element.

It is difficult to understand why reference is not made to the monograph **Analytical Chemistry of Titanium Metals and Compounds**, by Maurice Codell (also edited by P. J. Elving and I. M. Kolthoff). Surely, considering the brevity of the treatment here, the reader should be referred to the only book devoted entirely to the analysis and determination of titanium. Furthermore, no reference is made to the work of J. C. White on the extraction and determination of the titanium thiocyanate complex with tri-*n*-octyl phosphine oxide, the most nearly specific and sensitive method for titanium known to this reviewer. Finally, no reference is made to the inert gas fusion method for determining oxygen in titanium metal, a peculiar omission because of the fact that it was the application of this technique by the ASTM task force which "sold" the Leco oxygen analyser to the analyst.

It is unfortunate that the statement "there is no method known in which a quantitative separation of zirconium and hafnium can be obtained" was made so shortly before successful ion-exchange separations were performed by the U.S. Bureau of Standards and (independently of course) by the Russians. In Table IX, p. 92, it is stated that zirconium can be precipitated with *m*-nitrobenzoic acid and separated from thorium, in contradiction to the literature cited. A minor omission is the fact that Duval has reported that the zirconium oxide obtained when some compounds are ignited may be oxygen deficient.

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M. WILLIAMS

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presented in seven sub-sections by R. Goulden, W. Kirsten, A. S. Jones, A. M. G. Macdonald, F. H. Oliver and A. Sykes. Ingram then deals with the determination of functional groups, and the book closes with a description of titrations in non-aqueous solvents by T. S. West.

It is difficult to review the mass of information to be found here. Each half of the volume could well be regarded as a book in its own right. Many experts must, of course, have a hand in writing any modern work on analytical chemistry if each part of it is to receive really authoritative treatment; and perhaps it may not matter much whether the various sections so written are issued as separate monographs or are collected into a series of volumes such as these with an almost arbitrary selection in any one volume. There will be those who would prefer the chance of buying the sections in which they are most interested one by one and free from association with the apparently irrelevant material of other sections. On the other hand, such a method of publication would no doubt be most inconvenient for the publisher; and there is no gainsaying that the method adopted here tends to give volumes of more uniform size than the alternative would. But one cannot help wishing the present volume were not so heavy.

It is no adverse criticism to say that so far the work seems to be largely academic in outlook; that is to say, it deals in most instances with the pure substance and not with the impure material that is found in nature, admixed with other substances. It may well be argued that it is necessary to describe the fundamental aspects of the subject first, and later to proceed to the more complex question of the application of fundamentals to real life. This is the accepted procedure in other sciences, and it is a perfectly proper one to adopt here. We look forward to seeing how the editors will bring what they now publish into line with some of the problems that are most pressing to the industrial analyst who rarely has a pure substance, or, indeed, a simple one, to examine. Most analytical chemists have to spend far more time in getting their material into a condition in which the final method of determination can be applied in a valid manner and without vitiation of the result by the effect of extraneous influences than in making the actual determination itself. May one hope that future volumes will give more indication of the limitations of methods and of how to deal with interferences? But even if they do not, and the work remains predominantly restricted to the fundamental reactions and measurements involved in the discipline of analytical chemistry, with minor excursions into industrial work, it looks as though the whole work will fulfil the intentions of the editors. One's expectations are raised by this volume beyond the promise of the first; and one looks forward with keen expectation to what we shall see next.

K. A. WILLIAMS

Submicrogram Experimentation. Edited by N. D. CHERONIS. *Microchemical Journal* Symposium Series, Vol. I. Interscience Publishers Inc., New York and London, 1961. Pp viii + 351. $ 12.75.

THE textual material of this book reports the papers and discussions held at a symposium on this topic sponsored by The National Academy of Sciences—National Research Council (U.S.A.) and held at Arlington, Virginia, May 15th–18th, 1960. It is not practical to mention more than a few of the topics concerned, but the following give some indication of the scope of the symposium:—an inventory of problems unique to submicrogram experimentation, trace-element analysis (activation, emission-spectroscopy, flame-photometry, spectrophotometry, mass-spectroscopy and X-ray procedures), study of synthetic chemical elements by submicrogram techniques, microbiological assay and carcinogenicity, X-ray spectroscopy in biological systems, olefactory sensing methods, microscopy of small particles, gas-chromatography, cytochemistry and infrared microspectrophotometry.

There is a considerable amount of discussion of inconclusive matters such as the unit nomenclature to be adopted for $\leqslant 10^{-6}$ g amounts *etc.*, and one notes with amusement that one distinguished microchemist at least is uncertain as to which direction is "up" and which "down". The editing is factual and rather unimaginative in places, *cf.* p. 35 for a discussion on the policy of the New York Public Library on 42nd St. Topics not covered, or unsatisfactorily reported, include organic ultramicroanalysis on the microgram scale (ultimate and functional), electrochemical methods in general and catalytic procedures, surely essential in any discussion of submicrogram techniques, *cf.* however, the last four words of the final paper, p. 348. In general, the subject matter is rather heavily weighted in favour of biological topics and in this respect the reviewer found the sections on cytochemistry carcinogenicity, X-ray and infrared microspectrophotometry noteworthy for their interest. Most readers will also find the sections on spectrofluorimetry and phosphorimetry to be outstanding.

Summarising, it might be said that this is quite an interesting book with its main appeal lying in the reporting of many personal opinions and experimental observations. Apart from this interesting play of personalities, however, it is problematical whether or not the subject matter of the book makes an outstanding scientific contribution to the literature.

T. S. WEST.

presented in seven sub-sections by R. Goulden, W. Kirsten, A. S. Jones, A. M. G. Macdonald, F. H. Oliver and A. Sykes. Ingram then deals with the determination of functional groups, and the book closes with a description of titrations in non-aqueous solvents by T. S. West.

It is difficult to review the mass of information to be found here. Each half of the volume could well be regarded as a book in its own right. Many experts must, of course, have a hand in writing any modern work on analytical chemistry if each part of it is to receive really authoritative treatment; and perhaps it may not matter much whether the various sections so written are issued as separate monographs or are collected into a series of volumes such as these with an almost arbitrary selection in any one volume. There will be those who would prefer the chance of buying the sections in which they are most interested one by one and free from association with the apparently irrelevant material of other sections. On the other hand, such a method of publication would no doubt be most inconvenient for the publisher; and there is no gainsaying that the method adopted here tends to give volumes of more uniform size than the alternative would. But one cannot help wishing the present volume were not so heavy.

It is no adverse criticism to say that so far the work seems to be largely academic in outlook; that is to say, it deals in most instances with the pure substance and not with the impure material that is found in nature, admixed with other substances. It may well be argued that it is necessary to describe the fundamental aspects of the subject first, and later to proceed to the more complex question of the application of fundamentals to real life. This is the accepted procedure in other sciences, and it is a perfectly proper one to adopt here. We look forward to seeing how the editors will bring what they now publish into line with some of the problems that are most pressing to the industrial analyst who rarely has a pure substance, or, indeed, a simple one, to examine. Most analytical chemists have to spend far more time in getting their material into a condition in which the final method of determination can be applied in a valid manner and without vitiation of the result by the effect of extraneous influences than in making the actual determination itself. May one hope that future volumes will give more indication of the limitations of methods and of how to deal with interferences? But even if they do not, and the work remains predominantly restricted to the fundamental reactions and measurements involved in the discipline of analytical chemistry, with minor excursions into industrial work, it looks as though the whole work will fulfil the intentions of the editors. One's expectations are raised by this volume beyond the promise of the first; and one looks forward with keen expectation to what we shall see next.

K. A. WILLIAMS

Submicrogram Experimentation. Edited by N. D. CHERONIS. *Microchemical Journal* Symposium Series, Vol. I. Interscience Publishers Inc., New York and London, 1961. Pp viii + 351. $ 12.75.

THE textual material of this book reports the papers and discussions held at a symposium on this topic sponsored by The National Academy of Sciences—National Research Council (U.S.A.) and held at Arlington, Virginia, May 15th–18th, 1960. It is not practical to mention more than a few of the topics concerned, but the following give some indication of the scope of the symposium:—an inventory of problems unique to submicrogram experimentation, trace-element analysis (activation, emission-spectroscopy, flame-photometry, spectrophotometry, mass-spectroscopy and X-ray procedures), study of synthetic chemical elements by submicrogram techniques, microbiological assay and carcinogenicity, X-ray spectroscopy in biological systems, olefactory sensing methods, microscopy of small particles, gas-chromatography, cytochemistry and infrared microspectrophotometry.

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T. S. WEST.

Transactions of the Symposium on Electrode Processes. Edited by ERNEST YEAGER. John Wiley and Sons, Inc., New York, 1961, Pp. xiv + 374. 160/-.

THIS book contains the proceedings of the Symposium on Electrode Processes, held in Philadelphia from 4th to 6th May, 1959, under the Chairmanship of Professor P. Delahay, who has contributed a Foreword. The contributions to this meeting were limited to sixteen papers, delivered by authors selected to provide authoritative coverage of theoretical electrochemical topics of current interest. This procedure was adopted to provide sufficient time for discussion and for the contribution of unpublished material. The success of this approach is indicated by the very large amount of recorded discussion and communications to the Editor which appear in this volume. In addition to the invited papers two general discussions, entitled *Transient Methods for the Kinetic Study of the Electrodeposition of Metals* and *Adsorption at Electrodes*, are reported in detail. The range of topics discussed is very wide, but in general they fall into three classes: double layer phenomena and correlation with electrode processes; metal deposition and dissolution; and fast electrode reactions. In addition three papers dealt with the mechanism of the hydrogen electrode reaction, the effects of partial and complete isotopic substitution of H by D in aqueous solution, the rates of electrochemical hydrogen and oxygen evolution and certain other effects, and the kinetics of hydrogen evolution and dissolution at activated platinum electrodes. Other papers of interest were concerned with the determination of electrode reaction mechanisms from electrode reaction orders, theory of electron transfer processes at electrodes, and acousto-electrochemical effects in electrode systems. Notable omissions were papers on the subjects of polarography and anodic films, but it is pointed out that this was a matter of deliberate policy in view of recent International meetings devoted to these fields.

As might be expected from the list of distinguished contributors, the standard is very high, and this book is not for the reader without specialist knowledge in electrochemistry. Its contribution to the literature of the subject is, however, important and it will be a valuable work of reference. It is excellently produced in clear type, with good diagrams, and it is well bound. It is recommended to all those whose studies touch upon the deeper knowledge of electrochemical processes.

G. F. REYNOLDS

Monographies de Chimie Organique, Vol. IV. Microanalyse Organique Élémentaire, R. LÉVY, and **Determination des Masses Moléculaires et des Degrés de Polymérisation,** P. PIGANIOL, H. JEAN, G. VALLET, and C. WIPPLER. Masson et Cie, Paris, 1961. Pp. vi + 428 with 124 figs. P. 72 NF (cloth), 82 NF (boards)

THE 23 volume *Traite de Chimie Organique* which was completed in 1955 deals very briefly with several topics which now command greater attention. The present book is the fourth volume of a new complementary series which will deal more adequately with selected topics. In the initial monograph, a 226-page survey of methods for the detection and determination of the elements present in organic and organo-metallic compounds, Levy has combined material from 625 references to give an excellent review. It is extremely unfortunate that some of the value of this section is lost through what appears to be a delay in publication—the bibliography is complete only up to the end of 1956. Nevertheless the wide scope of the review and the manner in which the author has incorporated the essential details of the various methods and their modifications make it an asset to the research worker. The elements are treated systematically in the usual order, due reference being made to both conventional and to other rather more specialised methods such as the submicro determination of the elements and the determination of radioactive isotopes. The remainder of the book is concerned with the determination of molecular weights, with particular reference to polymeric materials, the rather unusual combination of monographs probably arising because this book is part of a series. All the conventional methods of determining the molecular weight distribution of high polymers are described although some are given in much greater detail than others. The general impression created by this section is that although the reviews are well written they are not up-to-date and far too much attention is paid to methods which now are only of historical interest. As an example of this tendency the section dealing with ebulliometry describes apparatus which is not only unsatisfactory for the measurement of the elevation of the boiling point produced by polymers but would in fact be too insensitive to permit the determination of the molecular weight of simple organic compounds. Conversely there is no mention of any of the new ebulliometers which have been described recently. This section cannot therefore be recommended either to the student or to the research worker.

A. D. CAMPBELL
J. R. MAJER

Talanta, 1962, Vol. 9, pp. 469 to 471 Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

(Material for this section should be sent directly to the Associate Editor)

IVAN PAVLOVICH ALIMARIN, who recently became U.S.S.R. Regional Editor of TALANTA (see *Talanta*, 1962, **9**, *facing* 189), was born on the 11th of September, 1903, in Moscow. He graduated from the Higher Educational Establishment in 1928. In 1935 he became Dozent, and in 1950 Doctor of Chemical Sciences and Professor. In 1953 he was elected a Corresponding Member of the U.S.S.R. Academy of Sciences.

Professor Alimarin is an Honourable Member of the Analytical Chemistry Group of the Society of Industrial Chemistry of France (1959), a Member of the Analytical Chemistry Section Committee of I.U.P.A.C. (1959), a Member of the Commission on Nomenclature. He is also the President of the Analytical Chemistry Commission of the U.S.S.R. Academy of Sciences. During 1929–53 he worked as Dozent and Professor of Analytical Chemistry at the Moscow Institute of Fine Chemical Technology. From 1953 up to the present time he is Professor of Analytical Chemistry at the M. V. Lomonosv Moscow State University, and he also works at the V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry of the U.S.S.R. Academy of Sciences.

The principal trends of Professor Alimarin's research work are the development of theoretical problems and new methods of analysis of rare elements, and the use of radioactive isotopes in chemical analysis. In addition, a number of investigations have been carried out in the field of ultramicro analysis. He has published 280 papers and 3 manuals in analytical chemistry.

CZECHOSLOVAKIA

June: **Quantometric Methods in Analytical Chemistry:** *Association for Spectral Analysis*, Ostrava

DEUTSCHE DEMOKRATISCHE REPUBLIK

Jahreshaupttagung der Chemischen Gesellschaft in der Deutschen Demokratischen Republik vom 21.–24. November 1962 in Leipzig.

Thema: **Methoden und Anwendungen der Strukturchemie.**

Das Program umfaßt Plenarvorträge und Sektionshaupt- und Kurzvorträge. Es sollen insbesondere die modernen Methoden der chemischen Strukturforschung (Röntgenstrukturanalyse, Spektralanalyse, elektrische Meßverfahren) behandelt werden.

Parallel zu dieser Tagung findet sie Vortragstagung des Fachverbandes Lebensmittelchemie statt. Es werden Themen aus dem Gebiet der Lebensmittelchemie und -analytik behandelt.

Wietere Auskunft ist von das Sekretariat der Chemischen Gesellschaft in der DDR, Berlin W8, Unter den Linden 68/70, zu erhalten.

FRANCE

La Commission de Terminologie (C.I.T.) du **Comité International de la Détergence** s'est réunie, pour le 7 ème fois, a Rotterdam (Pays-Bas) les 8 et 9 Mars 1961, sous la présidence de Monsieur COMBETTE (France).

La Commission a décidé la constitution de Groupes de Travail, dont l'un en particulier a été chargé d'étudier la mise sur pied d'un classement simplifié des agents de surface, dérivant du classement scientifique précédemment élaboré.

Par ailleurs, la Commission a adopté toute une série de définitions de termes du domaine des agents de surface. Celles d'entre elles qui ont déjà subi l'épreuve de la seconde lecture seront soumises pour homologation internationale, à *L'Organisation International de Normalisation* "*I.S.O.*".

WEST GERMANY

Wednesday–Saturday 13–16 June 1962: Fourth International Symposium on Gas Chromatography—Forty-first Meeting of European Federation of Chemical Engineering: Analytical Chemistry Division, Gesellschaft Deutscher Chemiker and Gas Chromatography Discussion Group, Hydrocarbon Research Group of Institute of Petroleum, Hamburg (see Talanta, 1962, 9, 399).

Sunday–Friday 26–31 *August* 1962: **Thirteenth Session of the International Commission for Uniform Methods of Sugar Analysis.** Hamburg (see *Talanta*, 1962, **9**, 401).

A session is held every fourth year and the programme is designed to deal with all aspects of sugar analysis, including starch hydrolysis products. The session provides a suitable platform for reports on and ample discussion of the latest developments in the field by both academic and industrial experts representing more than twenty countries.

UNITED KINGDOM

Wednesday 27 *June* 1962: **Discussion Meeting:** *Microchemistry Group, Society for Analytical Chemistry. The Feathers*, Tudor Street, London, E.C.4. 6.30 p.m.

Wednesday–Wednesday 10–17 *July* 1963: **XIXth International Congress of Pure and Applied Chemistry.** London.

The Congress will follow the XXIInd Conference of the International Union of Pure and Applied Chemistry, 5–9 July, 1963, also in London.

The scientific programme of the Congress will consist of some 20 invited congress lectures in addition to a wide range of contributed papers. These papers will be presented in the following divisions:

A. *Organic Chemistry*
B. *Inorganic Chemistry*
C. *Analytical Chemistry*
D. *Applied Chemistry*

of which the division of Organic Chemistry will form the main theme of the Congress. The specific topics to be discussed in the division of Analytical Chemistry are:

1. *Trace Analysis*
2. *Separation Methods*
3. *Electroanalysis*
4. *Teaching of Analytical Chemistry.*

Only papers that have a direct bearing on the programme topics can be considered and the number accepted for reading at the meeting will be strictly limited. All correspondence concerning the Congress should be addressed to the Honorary Secretary, XIXth International Congress of Pure and Applied Chemistry, 14, Belgrave Square, London, S. W. 1, England. All correspondence concerning the Conference should be addressed to: Dr. RUDOLF MORF, Secretary General of I.U.P.A.C. c/o Hoffmann La Roche & Co. Ltd., Basle 2, Switzerland.

The following *New British Standard* is announced by **British Standards Institution:**

B.S. 3450: 1962: Method for the quantitative chemical analysis of binary mixtures of acrylic and certain other fibres. This provides a method for determining the proportions of fibre in binary mixtures of acrylic fibres with wool, silk, polyamide, polyester and viscose rayon fibres. It is not applicable to acrylic fibres dyed with pre-metallized or after-chrome dyes. It is suitable for application to fibres in any textile form, *e.g.* tow, sliver, roving, yarn or fabric. (Price 4s. 6d.)

The following *Amendment Slips* are also announced:

B.S. 1005: 1942: Sampling and analysis of high purity zinc and zinc alloys for die casting. Amendment No. 1: PD 4464.

B.S. 1728: Methods for the analysis of aluminium and aluminium alloys: Part 3: 1952: Zinc (mercuric potassim thiocyanate method). Amendment No. 1: PD 4466.

B.S. 1016: *Methods for the analysis and testing of coal and coke: Part* 16: 1961: *Reporting of results. Amendment No.* 2: *PD* 4425.

B.S. 1121: *Methods for the analysis of iron and steel: Part* 33: 1955: *Iron in ores, slags and refractories. Amendment No.* 4: *PD* 4439.

B.S. 2782: *Methods of testing plastics: Part* 5: 1958: *Miscellaneous methods. Amendment No.* 6: *Methods* 502 *water absorption and water soluble matter: PD* 4447.

UNITED STATES OF AMERICA

Sunday–Friday 3–8 *June* 1962: **Tenth Annual Meeting:** *A.S.T.M. Committee E*-14 *on Mass Spectrometry.* New Orleans, La.

Monday–Wednesday 4–6 *June* 1962: **Nuclear Congress and Atomic Exposition:** *Engineers Joint Council, Inc.* New York Coliseum.

Monday–Friday 11–15 *June* 1962: **Symposium on Molecular Structure and Spectroscopy.** Department of Physics and Astronomy, Ohio State University, Colombus 10, Ohio.

Monday–Friday 18–22 *June* 1962: **International Conference on Spectroscopy,** also designated **Xth Colloquium Spectroscopium Internationale:** *Society for Applied Spectroscopy.* University of Maryland, College Park, Md., near Washington D.C. (see *Talanta*, 1961, **8**, 914).

Sunday–Friday 24–29 *June*: **65th Annual Meeting of A.S.M.T.** Statler Hilton Hotel, New York City.

Wednesday–Friday 13–15 *June* 1962: **Analytical Automation and Data Processing:** *Annual Summer Symposium of Division of Analytical Chemistry, A.C.S.* and *Analytical Chemistry.* College Park, Maryland (see *Talanta*, 1962, **9**, 338).

The final programme contains the following minor alterations and additions:

J. P. STRANGE	*Sensors for Automatic Analyses.*
R. BULL	*A New Instrument for Automated Analysis of Liquid Samples.*
W. J. BLAEDEL and G. P. HICKS	*Automatic Enzyme Procedures.*

Tuesday–Thursday 9–11 *October* 1962: **Sixth Conference on Analytical Chemistry in Nuclear Reactor Technology** and **Third Conference on Nuclear Reactor Chemistry:** *Oak Ridge National Laboratory.* Gatlinburg, Tennessee.

Subjects to be considered at the Conference on Analytical Chemistry in Nuclear Reactor Technology include: the use of isotopes in analytical chemistry; instrumentation; analysis of organic moderators; spectroscopy; analytical developments in radiochemistry and nucleonics.

Papers of interest to analytical chemists on the aforementioned topics or closely related subjects, including review papers, are solicited. Authors should submit an abstract of 400–600 words on their papers not later than June 4. Presentation time limit is 20 min. Abstracts and enquiries for analytical chemistry should be directed to C. D. SUSANO, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tennessee, U.S.A.

Talanta, 1962, Vol. 9, p. 472. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Analytical applications of infrared spectroscopy: M. AL-KAYSSI and R. J. MAGEE. (2 *March* 1962).

Chelating action of thioglycollic acid with silver and some common divalent cations: Miss A. M. CABRERA and T. S. WEST. (5 *March* 1962).

The chronopotentiometric behaviour of antioxidants and antiozonants at the graphite electrode: G. A. WARD. (5 *March* 1962).

Spectrophotometric determination of palladium and platinum with dibenzyldithio-oxamide: JOHN T. PYLE and WILLIAM D. JACOBS. (5 *March* 1962).

The spectrophotometric determination of sulphur in iron alloys (methylene blue method): OWEN H. KRIEGE and ARTHUR L. WOLFE. (12 *March* 1962).

A new reductometric reagent-iron^{II} in strong phosphoric acid medium: Titration of uranium^{VI} with iron^{II} at the room temperature: G. GOPALA RAO and SEETARAMARAJU SAGI. (12 *March* 1962).

The determination of traces of arsenic and antimony in samples of platinum by neutron-activation analysis: R. A. KILLICK and D. F. C. MORRIS. (13 *March* 1962).

The ultraviolet spectra of chlorine and its oxides in carbon tetrachloride: ZDENEK SPURNY. (14 *March* 1962).

Titrimetric analysis with chloramine-T: Part VIII: The chloramine-T-thallium^{I} and thiocyanate reactions and some further applications employing excess of reagent: E. BISHOP and V. J. JENNINGS (15 *March* 1962).

Studies on uronic acid materials, V: The thermal decarboxylation method of analysis: D. M. W. ANDERSON, S. GARBUTT and J. F. SMITH. (15 *March* 1962).

Precipitation of nickel dimethyglyoximate from homogeneous solution: E. D. SALESIN, E. W. ABRAHAMSON and LOUIS GORDON. (16 *March* 1962).

Separation of mercury by extraction with tri-n-butyl phosphate: D. F. C. MORRIS and J. H. WILLIAMS. (20 *March* 1962).

Complexometric determination of copper in presence of other ions: O. B. BUDEVSKY and L. SIMOVA. (20 *March* 1962).

The hydrolysis of 8-acetoxyquinoline: DAVID ELLIOTT, LESTER C. HOWICK, BILLY G. HUDSON and WILLIAM K. NOYCE. (16 *March* 1962).

Untersuchungen über die Reaktionsfahigkeit von Chrom und Titan mit Pyrrolidindithiocarbaminat: H. MALISSA and H. KOTZIAN. (20 *March* 1962).

Determination of antimony in lead by neutron-activation analysis: F. ADAMS and J. HOSTE. (21 *March* 1962).

Pyrohydrolytic determination of fluoride in milligram quantities of plutonium fluorides: G. S. RAO and M. S. SUBRAMANIAN. (22 *March* 1962).

The determination of phosphorous in hypereutectic silicon/aluminium alloys by a neutron activation method: R. BLACKBURN and B. PETERS. (23 *March* 1962).

Studies in ammonium hexanitratocerate as an oxidimetric reagent titration of oxalic and mandelic acids at the room temperature: G. GOPALA RAO, P. V. KRISHNA RAO and K. S. MURTY. (27 *March* 1962).

ERRATA—VOLUME 9

Page 85: reference 1 should read *G. Frederick Smith, Talanta*, 1962, **9**, 65.

Page 176: the legend for Fig. 1 is under Fig. 2 and *vice versa*.

Page 328: the legend for Table II should read *Determination of copper in presence of nickel^{II} and iron^{III}*.

Talanta, 1962, Vol. 9, pp. 473 to 481. Pergamon Press Ltd. Printed in Northern Ireland

DETERMINATION OF ALKYL CELLULOSE ETHERS BY GAS CHROMATOGRAPHY

JOHN G. COBLER*, E. PAUL SAMSEL* and GARTH H. BEAVER†
The Dow Chemical Company, Midland Division, Midland, Michigan, U.S.A.

(*Received* 10 *October* 1961. *Accepted* 8 *November* 1961)

Summary—A gas chromatographic technique for the quantitative determination of mixed alkoxyl groups in cellulosics is presented. The procedure consists of reacting the alkoxyl constituents with hydriodic acid by a modified Zeisel method. The alkyl iodides thus formed are collected in a cold trap containing 2,2,5-trimethylhexane as a solvent. An aliquot of this solvent containing the alkyl iodides is subsequently analysed by gas chromatography. Known compounds containing methoxyl-, ethoxyl- and isopropoxyl groups are used as standards. Experimental and commercially available methylcellulose, ethylcellulose, ethylmethylcellulose, and hydroxypropylmethylcellulose have been analysed by this procedure. Results are compared with those obtained by other alkoxyl methods. The method provides a direct means for the simultaneous determination of mixed alkyl substituents in cellulose or related polysaccharides. Indirect methods requiring multiple determinations on the same sample and cumbersome fractional precipitation procedures are unnecessary.

DETERMINATION of the alkoxyl substituent of a cellulose compound commences with the classical hydriodic acid decomposition procedure of Zeisel.[1] The corresponding alkyl iodides thus formed are swept from the reaction mixture with nitrogen. Modifications or improvements of the Zeisel method may be divided into the following general areas: (1) gravimetric, (2) titrimetric, (3) differential solubility adaptations, and (4) instrumental adaptations including gas chromatography and infrared spectrometry.

There has been some interest in the absorption and combustion method of Friedrich[2] since it was first published in 1929. Hozumi[3] modified Friedrich's method by absorbing the distilled alkyl iodide on porous silver granules, then heating to decompose the alkyl iodide and absorption of the iodine on the silver. Fukuda[4] used the Zeisel method for decomposition, then subjected the alkyl iodide product to combustion over a platinum catalyst in an air stream to form iodine and carbon dioxide.

Samsel and McHard[5] modified the apparatus and technique of the Vieböck and Brecher[6] titrimetric method. Recently, Cundiff and Markunas[7] presented another titrimetric method for the determination of alkoxyl groups, whereby the alkyl iodide was absorbed in pyridine and titrated directly with tetrabutylammonium hydroxide. They extended their work so that it would also apply to the analysis of higher alkoxyl groups such as propoxyl or butoxyl.

Separations of mixed alkyl substituents have always been difficult. Classically, Willstätter and Utzinger[8] separated methyl iodide from ethyl iodide on the basis of the differential solubility in absolute alcohol of tetramethylammonium iodide and trimethylethylammonium iodide. Makens, Lothringer and Donia[9] also formed the trimethylethylammonium iodide and the tetramethylammonium iodide, but separated them by differences in their solubility in a trimethylamine-nitrobenzene solution.

* Polymer Analysis Laboratory.
† Cellulose and Plastics Laboratory.

Sobue, Hatano and Arai[10] used a spectrophotometric technique to detect the presence of an alkyl iodide absorbed in pyridine. Anderson and Duncan[11] decomposed the alkoxyl-containing compounds by the Zeisel method, and used quantitative vapour phase infrared spectrometry to simultaneously determine the methoxyl or ethoxyl groups as the corresponding alkyl iodide.

With the developement of a practical instrumental gas chromatographic apparatus by Gohlke,[12] and the work of James and Martin,[13] which demonstrated that alkyl halides could be separated by gas chromatography, new improvements in the alkoxyl determination became possible.

Vertalier and Martin[14] decomposed the alkoxyl compound by the Zeisel technique, and used gas chromatography as a qualitative and semi-quantitative technique for alkoxyl determinations. They trapped the distilled alkyl iodide in a glass tube at dry ice temperature. Losses were reported at 25–50% of the theoretical value. However, their losses were constant as a function of the particular sample being decomposed. Kratzel and Gruber[15] separated alkyl halides by gas chromatography. They used the chromatograms for qualitative work, but felt that the condensation and subsequent vaporisation of the alkyl halides was unreliable for quantitative work. Kratzel and Gruber collected the individual alkyl iodides as they left the gas chromatographic column in the conventional bromine-glacial acetic acid-sodium acetate solution and titrated each fraction by the method of Vieböck and Brecher.[6]

Haslam, Hamilton and Jeffs[16] used gas chromatography to quantitatively determine acrylate esters which had been reduced to the alkyl iodide by the Zeisel technique. They incorporated known quantities of methyl chloride and ethylene dichloride with the mixture of trapped alkyl iodides, and used ratios of peak heights to quantitatively determine the alkyl iodides present.

In the present paper cellulosic- or polysaccharide-type compounds containing alkoxyl or mixed alkoxyl constituents are decomposed with hydriodic acid to form the corresponding alkyl iodides. The iodides are then removed from the reaction mixture by purging with nitrogen gas and are quantitatively absorbed in 2,2,5-trimethylhexane at a temperature of −80°. A portion of this solution containing the alkyl iodides is subsequently injected into a gas chromatographic apparatus. The areas under the various alkyl iodide peaks on the resulting chromatogram are compared with those obtained by the analysis of known compounds.

EXPERIMENTAL

Apparatus

Distillation apparatus (Fig. 1): This consists of a 50-ml side-arm flask, an air condenser with a scrubbing trap, an absorber trap, and an oil bath equipped with an electrical heating device so that the bath can be maintained at 150°.

Beckman gas chromatograph: GC-2A, with a 7-ft 1/4″ O.D. stainless steel tube column.

Absorbent: Di-2-ethylhexyl sebacate on firebrick (Absorbant No. 341-119, supplied by Burrell Corporation).

Microsyringe: 0·05-ml capacity.

Recorder.

Reagents

Methoxyl standard: *o*-Methoxybenzoic acid and/or *p*-methoxyphenol (Eastman Organic Chemicals).

Ethoxyl standard: *p*-Ethoxybenzoic acid (Eastman Organic Chemicals).

Propoxyl standard: 3-Isopropoxy-n-propylamine (American Cyanamid Co.).

2,2,5-Trimethylhexane: Pure grade (Phillips Petroleum Co.).
Phenol: Loose crystals, AnalaR.
Magnesium perchlorate: Anhydrous.
Helium gas.
Nitrogen gas.
Hydriodic acid: Constant boiling, reagent grade.

Conditions

The chromatographic apparatus is operated at 75°, using helium as the carrier gas at a flow rate of 68 ml/min. The recorder should have a range of 0–1 mV. The chart speed is 30 in. per hr. An attenuation of 50 is used for the methoxyl and /or ethoxyl determinations. When the simultaneous determination of methoxyl and hydroxypropoxyl substituents is performed, an attenuation of 50 is used for the methoxyl determination. After the methyl iodide peak has been recorded on the chromatogram, the attenuation should be changed to 2 for recording the isopropyl iodide peak. When large (60–80 mg) samples are analysed only for hydroxypropoxyl content, an attenuation of 5 is recommended.

Procedure

Place 3 ml of distilled water in the scrubbing trap (B) (see Fig. 1). Place a small amount of drying agent (magnesium perchlorate) into the inlet section of the absorber trap (E). With a hypodermic syringe, add 1 ml of 2,2,5-trimethylhexane to the outlet section of the absorber trap (E), and assemble the apparatus as shown in Fig. 1. Surround the trap (E) with a dry ice bath at −80°. To the reaction flask (C), add 2 g of phenol (loose crystals) and a few silicon carbide chips to prevent bumping. Add about 30 mg of sample, depending upon the alkoxyl content, and 6 ml of constant boiling hydriodic acid. Attach at once to the distillation apparatus, using a few drops of hydriodic acid to moisten the ground glass joint.

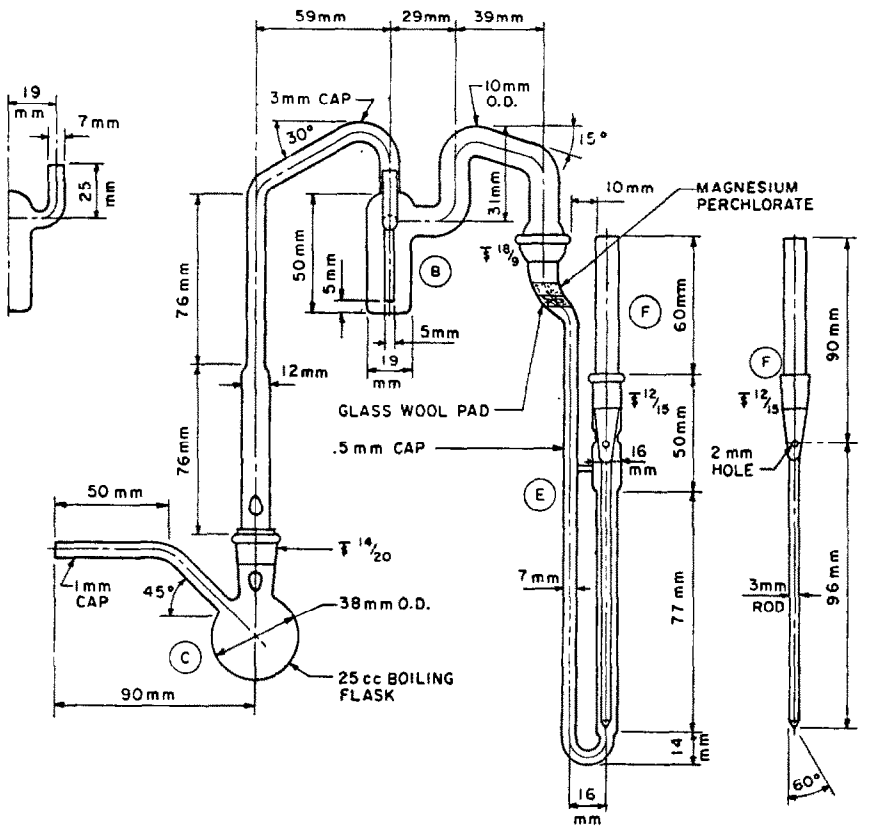


FIG. 1—Apparatus for alkyl iodide distillation and absorption.

Connect the side-arm to a source of nitrogen and pass the gas through the apparatus at the rate of 1–2 bubbles per sec. Immerse the reaction flask in an oil bath maintained at 150° and react for 1 hr. Upon completion of the hydrolysis, disconnect the absorber trap (E). By means of a microsyringe, immediately inject 0·05 ml of the 2,2,5-trimethylhexane solution containing the alkyl iodides into the gas chromatograph apparatus.

The concentration of the various alkyl iodides present in the 2,2,5-trimethylhexane will be recorded as the area under the corresponding peak on the chromatogram (Fig. 2). A blank determination on the apparatus and chromatograph column may be performed, although we have found the blank to be negligible.

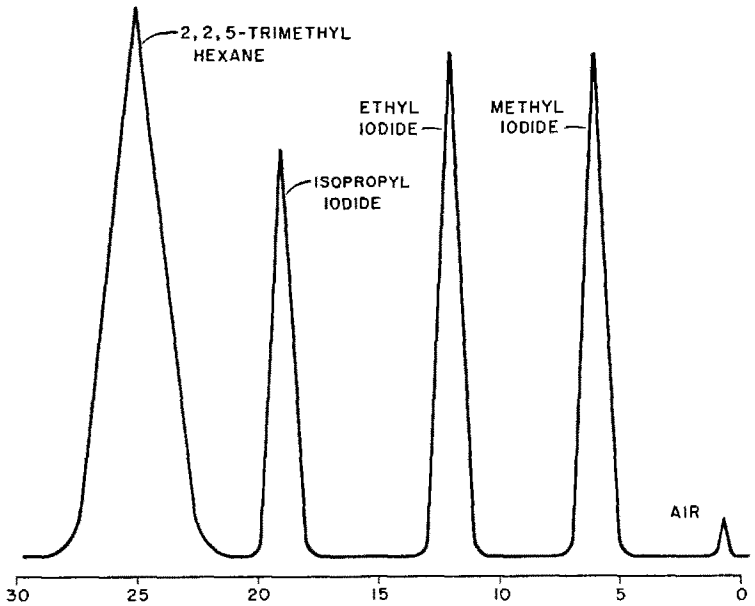


FIG. 2—Retention time in mins for alkyl iodides.
Column: 7ft, di-2-ethylhexyl sebacate
Flow rate: 68 ml of helium/min.
Temperature: 75°.
Current: 250 mA.
Chart speed: 30 in./hr.

Analysis of pure compounds should be performed by the method of Samsel and McHard,[5] and these results used to standardise the gas chromatographic method.

Once standardisation of the apparatus is accomplished by using various pure compounds, and a value obtained expressing mg of specific alkyl iodide per sq. cm. of chart area, this procedure may be used as a quantitative criterion.

Methoxyl analysis

o-Methoxybenzoic acid and *p*-methoxyphenol were used as methoxyl standards. A series of cellulose compounds containing methoxyl constituents was analysed as outlined under *Procedure*.

Ethoxyl analysis

p-Ethoxybenzoic acid was used as a standard. A series of ethoxyl-containing compounds was analysed by the procedure previously described.

Simultaneous methoxyl and ethoxyl analysis

Once chromatographic factors for methyl and ethyl iodide have been obtained, it is possible to simultaneously determine methyl and ethyl substituents in cellulose. A series of three mixed methylethylcelluloses was analysed using the previously described methoxyl and ethoxyl standards. In addition, a pure sample of β-methyltriethyl glucoside, prepared by A. W. Anderson of The Dow Chemical Company, was analysed.

Simultaneous methoxyl and hydroxypropoxyl analysis

3-Isopropoxy-n-propylamine was used as the isopropyl iodide standard. Analysis of this compound was performed by Samsel and McHard's method. A mass spectrographic analysis was also obtained on the halide decomposition products absorbed in the 2,2,5-trimethylhexane solvent. The previously discussed methoxyl standards were again used as methyl iodide reference materials. A series of commercially available mixed cellulose ethers containing methoxyl and hydroxypropoxyl substituents was analysed. An attenuation of 50 was used on the chromatograph recorder for the methyl iodide peak, while an attenuation of 2 was used for the isopropyl iodide peak.

DISCUSSION

Results for the determination of methoxyl substituents are presented in Table I. The methoxyl values obtained for both *o*-methoxybenzoic acid and *p*-methoxyphenol by the modified Zeisel method[5] agree with theoretical calculations. A series of cellulose compounds containing from 5% to 44·3% of methoxyl was analysed by

TABLE I—DETERMINATION OF METHOXYL SUBSTITUENTS ON CELLULOSE

Compound	Methoxyl, %	
	By gas chromatography	By modified Zeisel
o-Methoxybenzoic acid	20·3[1]	20·3
p-Methoxyphenol	25·1[1]	24·9
Methycellulose A	4·9– 5.1	5·3
B	14·4–14·8	14·5
C	16·8–16·9	17·0
D-1	28·5–28·7	28·8
D-2	30·6–30·9	30·9
D-3	29·1–29·7	30·0
E	44·2–44·3	44·5

[1] Theoretical

the gas chromatographic method, and these results are in agreement with those obtained by the modified Zeisel method. In all cases but Sample D-3, results obtained by the gas chromatographic method agree to within 0·5% of the value obtained by the modified Zeisel method.

Table II presents data on the determination of ethoxyl substituents. The value obtained for the standard *p*-ethoxybenzoic acid by the modified Zeisel method is the theoretical value. Here again, when the analyses of a series of ethylcellulose samples

TABLE II—DETERMINATION OF ETHOXYL SUBSTITUENTS ON CELLULOSE

Compound	Ethoxyl, %	
	By gas chromatography	By modified Zeisel
p-Ethoxybenzoic acid	27·1[1]	27·0
Ethylcellulose A	33·2–33·5	33·5
B	36·1–36·5	36·6
C	37·1–37·4	36·8
D	45·8–46·3	46·1
E	48·4–48·6	48·8
F	48·5–48·7	48·8
G	51·1–51·4	51·3
H	52·9–53·3	53·8

[1] Theoretical

by the gas chromatographic method and the method of Samsel and McHard are compared, excellent correlation and agreement are obtained. An exception is ethylcellulose Sample H where a low result was obtained.

Results on the simultaneous determination of methoxyl and ethoxyl cosubstituents in polysaccharides are presented in Table III. The analysis of β-methyltriethyl glucoside obtained by the gas chromatographic method agrees with the theoretical values of the compound. The sample of Edifas "A" was supplied by Imperial Chemical Industries Ltd. (ICI), and their method of analysis is unknown. Results obtained by the gas chromatographic analysis of this sample agree closely with the reported values as to total alkoxyl substitution, although the value reported by gas chromatography is higher in the case of methoxyl content than that reported by ICI. Methylethylcellulose, Samples D and E, were prepared by Dr. G. D. Mercer of The Dow Chemical Company. Dr. Mercer ethylated methylcellulose having initial methoxyl contents of 30% and 16%, respectively. The "comparative method" value reported in Table III for the ethoxyl content of methylethylcellulose, Samples D and E, was obtained by performing a total alkoxyl determination by the modified Zeisel method of the finished polymer. Additional substitution present above the starting methoxyl content was calculated as newly substituted ethoxyl groups. Results obtained by gas chromatography for the ethoxyl content of these mixed ethers indicate more ethyl ether present than was calculated.

TABLE III—SIMULTANEOUS DETERMINATION OF METHOXYL AND ETHOXYL SUBSTITUENTS ON CELLULOSE

Compound	Methoxyl, %		Ethoxyl, %	
	Gas chromatography	Comparative method	Gas chromatography	Comparative method
β-Methyltriethyl glucoside	10·9–11·2	11·2[1]	48·1–48·5	48·6[1]
Edifas "A"	5·7– 6·0	5·6[2]	14·7–14·8	15·4[2]
Methylethylcellulose D	25·9–26·0	27·1[3]	17·0–17·4	15·0[3]
E	14·0–13·8	13·9[3]	23·3–23·7	21·5[3]

[1] Theoretical.
[2] Value reported by Imperial Chemical Industries Ltd.—method used unknown.
[3] By difference, based on total alkoxyl substitution.

Data on the simultaneous determination of methoxyl and hydroxypropoxyl substituents on cellulose are presented in Table IV. The standard, 3-isopropoxy-n-propylamine, had an isopropoxyl content of 49·7% by the modified Zeisel method, compared with a theoretical value of 50·2%. The (corrected) methoxyl content of the mixed ethers in Table IV was calculated by determining the total alkoxyl by the modified Zeisel method, then subtracting the value for hydroxypropoxyl content obtained by the chromic acid oxidation method of Lemieux and Purves.[17] The modified Zeisel method and the chromatographic method agree closely as regards total alkoxyl substitution. However, gas chromatographic analysis for hydroxypropoxyl substituents indicates a value of 80% of that value obtained by the chromic acid oxidation method. As a result, the methoxyl content, obtained by the modified Zeisel method, corrected by the chromic acid oxidation factor, is slightly lower than the gas chromatographic analysis for methoxyl content.

While isopropyl iodide is the alkyl iodide obtained by the hydriodic acid decomposition of 3-isopropoxy-n-propylamine, the analysis of the mixed cellulose ether is concerned with the determination of the hydroxypropoxyl substituent. A conversion factor was used to convert mg of isopropoxyl per sq. cm. of chart space to mg of hydroxypropoxyl per sq. cm. of chart space. This factor was 1·27.

TABLE IV—SIMULTANEOUS DETERMINATION OF METHOXYL AND HYDROXYLPROPOXYL SUBSTITUENTS ON CELLULOSE

Compound	Methoxyl, %		Hydroxypropoxyl, %	
	By gas chromatography	By modified Zeisel (corrected)	By gas chromatography	By chromic acid oxidation[1]
3-Isopropoxy-n-propylamine	—	—	50·2[2]	49·7[3]
Mixed ether—A	24·2–23·8	25·3	5·6– 5·4	6·9
B	27·6–27·2	26·7	5·1– 5·0	6·4
C	29·5–28·9	27·8	7·6– 7·2	10·1
D	30·5–30·2	28·7	6·9– 6·7	9·1
E	28·5–27·6	28·3	8·2– 8·5	11·2
F	21·8–21·7	19·9	13·0–11·7	15·6

[1] Method of Lemieux and Purves.
[2] Isopropoxyl, theoretical.
[3] Isopropoxyl by modified Zeisel.

There has been considerable concern as to whether quantitative amounts of isopropyl iodide result when the mixed hydroxypropylmethylcellulose is decomposed with hydriodic acid, or whether some propylene is formed. It is a known fact that when ethylene glycol is decomposed with hydriodic acid, both ethylene and ethyl iodide are formed. It was felt that the hydroxypropoxyl group might react similarly and both propylene and isopropyl iodide could be reaction products. However, mass spectrographic results indicate the absence of propylene as a decomposition product of the hydriodic acid hydrolysis of methylhydroxypropylcellulose. This indicates that quantitative yields of isopropyl iodide are being obtained from the hydroxypropylmethylcellulose mixed ethers. Anderson and Duncan[18] have shown that when glycerol is subjected to the reaction conditions of the Zeisel method that isopropyl iodide is the only product. No propylene is formed.

The fact that hydroxypropoxyl analyses by the gas chromatographic method are consistently lower than those analyses obtained by the chromic acid oxidation method of Lemieux and Purves, suggested additional experiments. The same cellulose ether compounds were analysed by varying their sample weight to determine whether the quantity of isopropyl iodide formed was constant as a function of the total sample weight added to the reaction flask. Results of this experiment are presented in Table V, wherein 30- and 70-mg samples of three hydroxypropoxylmethylcelluloses were evaluated. A recorder attenuation of 5 was used for this analysis. Results were in excellent agreement and well within experimental error. They indicate that for our purposes all hydroxypropoxyl substituents in the cellulose ether have been transformed into isopropyl iodide and that this iodide is quantitatively determined in the gas chromatographic apparatus.

CONCLUSION

A method for the simultaneous determination of mixed alkyl substituents on cellulose has been presented. Both the methylethylcellulose and the methylhydroxypropylcellulose mixed ethers have been quantitatively analysed for their alkoxyl substituents in a single determination. This new method affords a 50% time saving over a present method of analysis.

TABLE V—DETERMINATION OF HYDROXYPROPOXYL CONTENT BY VARYING SAMPLE WEIGHT

Compound	Hydroxypropoxyl, %	
	30-mg sample	70-mg sample
IV—C	7·6	7·3
IV—D-1	6·9	6·8
IV—D-1	6·7	6·7

Availability of other hydroxypropoxyl standard compounds should enable complete resolution of the differences discussed concerning the results presented in Table IV. Particularly, a pure isopropoxybenzoic acid compound should assist in completely resolving any remaining discrepancy.

This method could be easily adapted to the analyses of other mixed ethers of cellulose, such as methylhydroxybutylcellulose. Compounds of this type are known in experimental quantities and are considered laboratory curiosities.

This method may find adaptation in the analysis of compounds such as hydroxyethylcellulose. Further research is suggested using, perhaps, hydrobromic acid to decompose the cellulose ether.

Acknowledgement—The authors wish to thank L. A. Gibb of Imperial Chemical Industries, Limited, for furnishing the sample of methylethylcellulose, "Edifas A."

Zusammenfassung—Eine gaschromatographische Methodik zur quantitativen Bestimmung gemischter Alkoxylgruppen in Zellulosen wird beschrieben. Die Alkoxylgruppen werden mit Jodwasserstoffsäure nach einer modifizierten Zeisel-Methode zur Reaktion gebracht. Die gebildeten Alkyljodide werden in einer Kühlfalle mit 2,2,5-Trimethylhexan als Solvent aufgefangen. Ein aliquoter Teil der Lösung wird in einen Gaschromatographen analysiert. Bekannte Verbindungen, die Methoxyl-, Äthoxyl- und Isopropoxylgruppen enthalten werden als Standards benutzt. Im Labor erzeugte und käufliche Zellulosen, die die oben genannten Gruppen einzel und im Gemisch enthielten, wurden analysiert und die Resultate mit denen nach anderen Alkoxylmethoden erhaltenen verglichen. Die Methode bietet eine Möglichkeit zur direkten Bestimmung der Alkoxyde in gemischt substituierter Zellulose und ähnlichen Polysaccheriden. Indirekte Methoden benötigen Mehrfachbestimmungen und mühevolle fraktionierte Fällungsoperationen, die hier unnötig sind.

Résumé—Les auteurs présentent une méthode de dosage de mélanges de groupes alkoxyle dans les produits cellulosiques par chromatographie gazeuse. Le procédé consiste à faire réagir les constituants avec l'acide iodhydrique par une méthode de Zeisel modifiée. Les iodures d'alcoyle ainsi formés sont recueillis dans un piège froid contenant du 2,2,5-triméthylhexane comme solvant. Une partie aliquote de ce solvant contenant les iodures d'alcoyle est ensuite analysée par chromatographie gazeuse. Des composés connus contenant les groupements méthoxy, éthoxy et isopropoxy sont utilisés comme étalons. Les composés suivants préparés expérimentalement et disponibles dans le commerce sont analysés par cette méthode: méthylcellulose, éthylcellulose, éthyl-méthylcellulose et hydroxypropyl-méthylcellulose. Les résultats sont comparés avec ceux obtenus par d'autres procédés.

Cette méthode fournit un moyen direct de dosage simultané de mélanges de substituants alcoxyle dans la cellulose ou les polysaccharides qui s'y rattachent. Des méthodes indirectes nécessitant de multiples dosages sur le même échantillon et des procédés incommodes de précipitation fractionnée ne sont pas nécessaires.

REFERENCES

[1] S. Zeisel, *Monatsh.*, 1885, **6,** 989.
[2] A. Friedrich, *Mikrochem.*, 1929, **7,** 185.
[3] K. Hozumi, *J. Pharm. Soc. Japan*, 1959, **79,** 237.
[4] M. Fukuda, *Mikrochim. Acta*, 1960, 448.
[5] E. P. Samsel and J. A. McHard, *Ind. Eng. Chem., Analyt.*, 1942, **14,** 750.
[6] F. Vieböck and C. Brecher, *Ber.*, 1930, **63,** 3207.
[7] R. H. Cundiff and P. C. Markunas, *Analyt. Chem.*, 1961, **33,** 1028.
[8] R. Willstätter and M. Utzinger, *Annalen*, 1911, **382,** 148.
[9] R. F. Makens, R. L. Lothringer and R. A. Donia, *Analyt. Chem.*, 1959, **31,** 1265.
[10] H. Sobue, A. Hatano and T. Arai, *J. Soc. Text. Cellulose Ind. (Japan)*, 1959, **15,** 21.
[11] D. M. W. Anderson and J. L. Duncan, *Talanta*, 1961, **8,** 1.
[12] R. S. Gohlke, *Analyt. Chem.*, 1957, **29,** 1723.
[13] A. T. James, and A. J. P. Martin, *Biochem. J.*, 1954, **57,** v.
[14] S. Vertalier and F. Martin, *Chim. Analyt.*, 1958, **40,** 80.
[15] K. Kratzel and K. Gruber, *Monatsh.*, 1958, **89,** 618.
[16] J. Haslam, J. B. Hamilton and A. R. Jeffs, *Analyst*, 1958, **83,** 66.
[17] R. U. Lemieux and C. B. Purves, *Canad. J. Res.*, 1947, **B-25,** 485.
[18] D. M. W. Anderson and J. L. Duncan, *Talanta*, 1961, **8,** 241.

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AN AUTOMATIC ANALYSER FOR HYPOPHOSPHITE WITH PARTICULAR REFERENCE TO ELECTROLESS* PLATING SOLUTIONS

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Summary—An apparatus is described for the continuous automatic determination of hypophosphite in a complex electroless nickel-plating solution. After catalytic oxidation of the hypophosphite, the evolved hydrogen is burned and the flame temperature used as a measure of the hydrogen and hence of the hypophosphite. The results are unaffected by changes in concentration of other ions present in the solution. Temperature variations in the range 20° to 70° produce only minor effects.

INTRODUCTION

IN response to a request for a continuous automatic analyser for the hypophosphite content of an electroless nickel-plating solution, a survey of the existing methods of analysis for hypophosphite was carried out.

Initially the plating solution contains sodium hypophosphite (the reducing agent), nickel sulphate (the source of nickel), various organic acids[1] (to buffer the pH), sodium hydroxide (to bring the pH to the optimum value) and also certain minor constituents. The effects on the plating of some of the minor constituents have been investigated by Brenner and Riddell.[2] As the bath ages the hypophosphite and nickel are consumed, phosphite is formed and the pH drops; it is necessary, therefore, to add sodium hydroxide, sodium hypophosphite and nickel sulphate as plating proceeds, thus producing with time a concentration gradient of sodium phosphite and sodium sulphate.

In view of the complex and changing nature of the plant liquor, especially the build-up of phosphite which occurs in operation of the plant, the normal titrimetric methods of analysis for hypophosphite were considered to be unsuitable for an automatic process. The colour of the nickel-organic acid complex present in the plating solution was a factor to be taken into account if colorimetric methods were to be considered.

Palladium black acts as a catalyst in the decomposition of hypophosphite and consequently the possibility of developing a method of analysis based on this reaction was examined.

The reaction which occurs is the dehydrogenation of the hypophosphite ions[3,4] with formation of phosphite ions and hydrogen gas:

$$H(H_2PO_2) \xrightarrow{\text{catalyst}} HPO_2 + H_2 \qquad \text{(i)}$$

$$HPO_2 + H_2O \longrightarrow H_2(HPO_3) \qquad \text{(ii)}$$

The method would be truly continuous and the hydrogen might be measured in a variety of ways: (a) detection with a katharometer, (b) detection with a Hersch-type

* Electroless plating may be defined as an autocatalytic chemical reduction process for continuously plating a metal from a solution of the metal salt containing a reducing agent.

galvanic cell, (c) combustion of the hydrogen and measurement of the flame temperature with a thermocouple. Although methods (a) and (b) are both capable of very high sensitivities, method (c) can be much the simplest. For this reason it was chosen. The thermocouple was connected to a strip-chart recorder.

EXPERIMENTAL

The initial work on the development of this method was carried out using aqueous sodium hypophosphite solutions and a catalyst prepared by electroplating palladium on thin silver foil. However, when using plant liquor it was found that the rate of the reaction was greatly reduced thus necessitating the use of larger quantities of catalyst. The form of catalyst which was finally used was prepared by plating palladium on silver-plated copper gauze. The metals of Group VIII of the Periodic Table are catalytic at or near the boiling point of water. Palladium is an exception in that it is catalytic at room temperature. Most other metals will exchange with nickel in the plating bath, the deposited nickel being catalytic. It was found in practice that the palladium and the silver of the prepared catalyst both dissolved in the plating solution, depositing a form of nickel which was catalytic at room temperature. It was found that without the silver deposit on the copper, the palladium was not such an effective catalyst. No explanation of this fact could be discovered because neither copper nor silver alone would catalyse the reaction at room temperature. Once this deposit of nickel had formed, the activity of the catalyst remained constant.

In use, the activity of the catalyst fell off to near zero within a few hr but it could be revived by washing with ammonia solution, suggesting that the poisoning was caused by adsorption of the organic acid molecules on the active points of the catalyst. In order to prevent the catalyst from becoming poisoned, ammonium hydroxide solution (1N) was metered into the apparatus together with the plant liquor. The metering was accomplished in each case by a continuously variable micrometering pump. After approximately 9 months use the catalyst showed no signs of becoming poisoned under these conditions. Two pieces of catalyst are used in a U-shaped chamber and the analysis mixture flows down one limb and up the other, the evolved hydrogen being collected at the top and passed, via a spray trap, to the detector unit. The analysis mixture flows in and out of the catalyst chamber via U-tube seals to prevent loss of hydrogen. The inlet U-tube seal also acts as a mixing chamber for the ammonium hydroxide solution and the plant liquor.

The detection system consists of a copper-constantan thermocouple which is situated just above the flame. In an earlier apparatus a thermocouple with a very small junction was used in order to obtain maximum sensitivity. However, the trace was liable to occasional fluctuations of about 1% of the chart width in magnitude because of collapse of the foam which collected in the catalyst chamber. Since no way could be found to destroy the foam without introducing other difficulties, the junction of the thermocouple was made massive by soldering it to a piece of copper tubing, thus rendering the trace stable by increasing the thermal inertia of the couple. This resulted in a reduction of sensitivity by a factor of about one half. At the same time, by utilising the copper of a copper-to-glass seal it became possible to fix the position of the thermocouple quite accurately and rigidly in relation to the jet. The output from the thermocouple was fed directly into a 10-mV strip-chart recorder. A further improvement in the geometry of the detector unit was obtained by cutting to 2 mm in length the hypodermic needle used as the jet and arranging that the distance from the jet to the copper block housing the thermocouple was about 5 mm, greater distances resulting in a loss in sensitivity. In order to eliminate as far as possible the effects of incidental draughts the air inlet and flue gas outlets of the detector unit were fitted with baffles of stainless steel gauze discs; in use, these have proved to be adequate.

In the earlier experimental detector the flame was lit by dismantling the unit and applying a match. For operation on the plant this was obviously undesirable so that an ignition system was fitted in which a high voltage spark was caused to jump between two tungsten electrodes placed one on either side of the jet. There is an additional advantage in that this system can be operated from a remote point with no possibility of disturbing the geometry of the detector. The spark is generated by a 12-V car ignition coil, power being supplied by two 9-V grid bias batteries in series. A bell push completes the circuit. The spark jumps the gap when the primary circuit is broken. The catalyst chamber and detector system are shown in Fig. 1.

Preparation of the catalyst

A sheet of copper gauze (40 mesh, 8″ × 11″) was rolled into a tight cylinder and cleaned by immersion in nitric acid (3*N*), then washed with distilled water. The cylinder was silver plated in a cyanide bath (2% silver nitrate solution plus sufficient 10% potassium cyanide solution to redissolve the silver cyanide precipitate) using a platinum wire anode wound on the cylinder and insulated from it by porcelain leads. The silver coated gauze and anode assembly was then transferred to a 2%

w/v palladium^{II} chloride solution in 0·2*N* hydrochloric acid and electroplated using a potential of 4V. The electrolysis was continued until a heavy deposit of palladium had formed.

The gauze could not be plated and then rolled because the deposit was only loosely adherent and would have been removed in the rolling operation. After standing for a few hr in the plant liquor/ammonium hydroxide solution mixture the catalyst had become nickel plated and its activity was then constant.

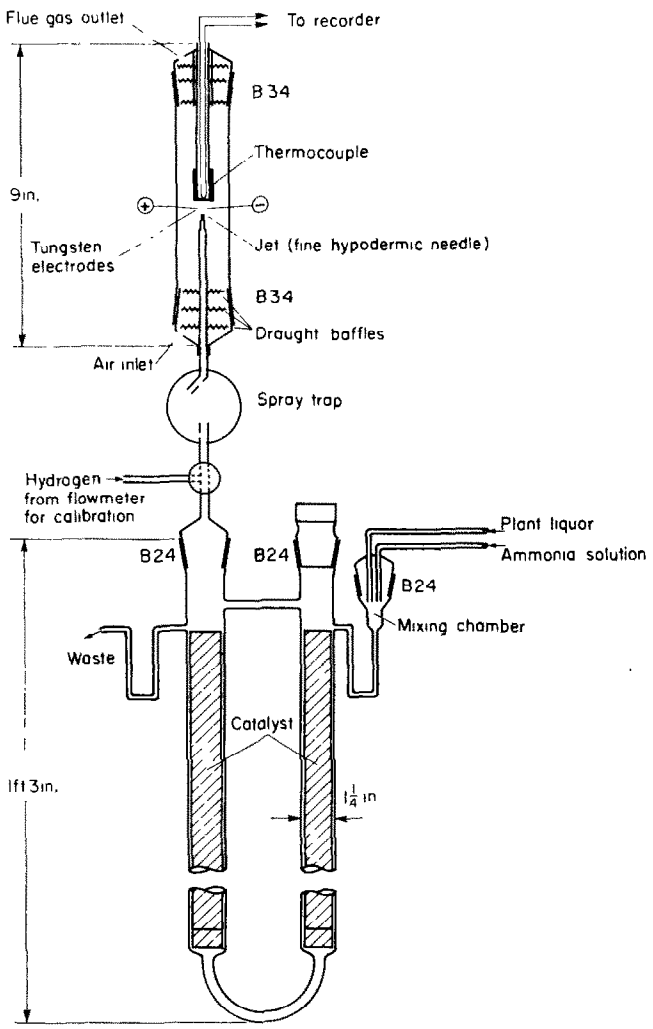


FIG. 1—Catalyst chamber and detector unit (not to scale).

RESULTS AND DISCUSSION

The apparatus described is capable of continuously analysing electroless nickel-plating solution for hypophosphite content. The most common concentration of hypophosphite is about 2%; the current calibration covers the range 1·5% to 3% but this can readily be altered, there being much latitude in the choice of flow rates, quantity of catalyst, and, for high concentrations, alteration in the sensitivity of the recorder. Where much lower concentrations of hypophosphite are concerned another detector, either of the Hersch-type or a katharometer, might be used. Fluctuations in

the concentrations of the other constituents of the plant liquor are without effect on the results obtained.

Since the plant operates at about 95° the temperature of the liquor at the sample point may vary; however, this causes only minor variations in the results obtained, an increase of about 1·5% of the reading occurring for every 10° rise in temperature in the range 20° to 70°.

Since the catalyst is only about 75% efficient in the present arrangement, the apparatus must be standardised against synthetic plant liquors of known hypophosphite content. Experience indicates, however, that even for the most stringent plant control the standardisation need only be checked once per week.

TABLE I—EFFECTS OF VARIATIONS OF THE FLOW RATES OF PLANT LIQUOR AND AMMONIUM HYDROXIDE SOLUTIONS

Plant liquor flow rate, *ml. min*$^{-1}$	1·5	2·0	3·0	4·0	5·0	5·7	4·0	4·0	4·0
Ammonium hydroxide solution flow rate, *ml. min*$^{-1}$	5·0	5·0	5·0	5·0	5·0	5·0	5·0	2·0	5·0
Reading, *chart divisions*	0	38	51	59	61	62	57·5	58	58

The time taken to indicate an instantaneous change of 0·5% of sodium hypophosphite monohydrate is about 15 min, 45 min being required for attainment of the final steady reading which is approached in an asymptotic manner.

The effects of variation of flow rates of the plant liquor and ammonium hydroxide solution are shown in Table I.

From this table it can be seen that much latitude is permissible in the choice of flow rates for the two liquids; 4·0 ml. min^{-1} for the plant liquor and 5·0 ml. min^{-1}

TABLE II—EFFECTS OF VARIATION OF NICKEL SULPHATE CONCENTRATION IN A SOLUTION COMPOSED OF 2% SODIUM HYPOPHOSPHITE MONOHYDRATE, SODIUM HYDROXIDE, ORGANIC ACIDS AND MINOR CONSTITUENTS

$NiSO_4 \cdot 7H_2O$, %	1·5	2·0	2·5
Reading, *chart divisions*	35·5	36	35·5

for the ammonium hydroxide solution were the values chosen for normal working.

Tables II and III show the results of variations in the concentrations of some of the constituents. Because sodium phosphite and sodium sulphate are formed in the plant at the same time their effects were determined together.

Calibration of the apparatus was carried out using synthetic plant solutions of known sodium hypophosphite content, the results being shown in Fig. 2. Also shown in Fig. 2 are the results of a calibration carried out using hydrogen gas from a cylinder. The gas was passed through a mixture of plant liquor and ammonium hydroxide

TABLE III—EFFECTS OF VARIATIONS OF SODIUM PHOSPHITE AND SODIUM SULPHATE CONCENTRATIONS IN A SOLUTION COMPOSED OF 2% SODIUM HYPOPHOSPHITE MONOHYDRATE, 2·5% NICKEL SULPHATE HEPTAHYDRATE, SODIUM HYDROXIDE, ORGANIC ACIDS AND MINOR CONSTITUENTS

$NaH_2PO_2 \cdot H_2O$, %	0	6·0	12·0	18·0
$Na_2SO_4 \cdot 10H_2O$, %	0	5·0	10·0	15·0
Reading, *chart divisions*	35·5	35	35	35

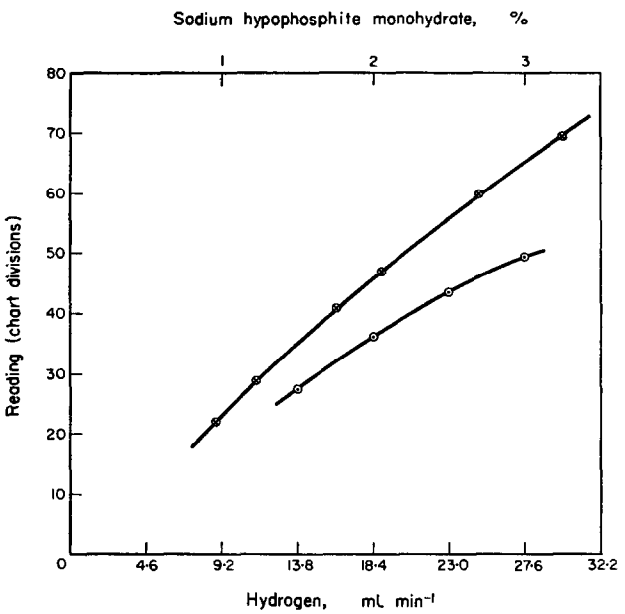


FIG. 2—Calibration graph (solution: 2% nickel sulphate heptahydrate, organic acids and minor constituents):
—○—○— calibration against sodium hypophosphite monohydrate,
—⊗—⊗— calibration against hydrogen.

TABLE IV—CATALYST EFFICIENCY

$NaH_2PO_2 \cdot H_2O$, %	1·5	2·0	2·5	3·0
Hydrogen (theoretical), *ml. min*$^{-1}$	13·8	18·4	23·0	27·5
Hydrogen (actual), *ml. min*$^{-1}$	10·7	14·2	17·1	19·7
Catalyst efficiency, %	78	77	75	72

solution flowing at the normal rates, then through a soap film flow meter and finally into the detector unit.

From the results shown in Fig. 2 the efficiency of the catalyst was calculated for several concentrations of hypophosphite (see Table IV).

Zusammenfassung—Ein Apparat zur kontinuierlichen, automatischen Bestimmung von Hypophosphit in einer Nickelplatierungslösung wird beschrieben. Nach katalitischer Oxydation des Hypophosphits wird der gebildete Wasserstoff verbrannt und die Flammtemperatur als Mass für den Gehalt gemessen. Die Ergebnisse werden durch Änderungen der Konzentration anderer anwesender Ionen nicht beeinflusst. Temperaturänderungen zwischen 20 und 70° haben nur geringen Einfluss.

Résumé—Les auteurs décrivent un appareil qui permet le dosage automatique continu des ions hypophosphite dans une solution complexe de revêtement de nickel non électrolytique. Après oxydation catalytique de l'hypophosphite, l'hydrogène dégagé est brulé; la températures de la flamme est utilisée comme mesure de la teneur en hydrogène. Les variations de concentrations des autres ions présents dans la solution n'influent pas sur les résultats. Des variations de températures dans le domaine de 20 à 70° n'ont pas d'effet important.

REFERENCES

[1] G. Gutzeit, *Trans. Inst. Met. Finishing*, 1956, **33**, 1.
[2] A. Brenner and G. Riddell, *J. Res. Nat. Bur. Stand.*, 1947, **39**, RP 1835.
[3] H. Wieland and A. Winkler, *Ann.*, 1923, **434**, 198.
[4] W. Franke and J. Moench, *ibid.*, 1942, **550**, 1.

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INDIRECT DERIVATOGRAPHIC DETERMINATION OF CALCIUM, STRONTIUM AND BARIUM IONS IN THE PRESENCE OF ONE ANOTHER

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Summary—For the determination of calcium, strontium and barium in one sample, they are precipitated together in the form of the mixed oxalate hydrates. An aliquot of the precipitate is treated in a derivatograph fitted with a furnace that can be heated to 1150°. From the curves which result, the following values are obtained: precipitate weight, weight of carbon dioxide formed in the decomposition of calcium carbonate and weight of carbon dioxide formed in the decomposition of strontium carbonate. From these three values, the amounts of calcium, strontium and barium in the sample can be calculated. The values used for the calculations were chosen from five values after an evaluation of the possible errors.

IN a previous communication[1] we reported an indirect derivatographic determination of calcium, strontium and barium ions. The basis of the method is to precipitate these ions in the form of oxalates, and under thermal decomposition we measured the total weight of precipitates and the weights of water (of crystallisation) and carbon dioxide formed and removed during the process. More recent investigations have shown that the method can be improved if the derivatographic measurement is finished at a higher temperature, at about 1100°, and the weight of carbon dioxide, formed in the thermal decomposition of strontium carbonate, is also measured.

EXPERIMENTAL

Reagents

Calcium chloride, strontium chloride, barium chloride: 0·05 *M* solutions were prepared from analytically pure reagents. Their accurate concentrations were determined by the Winkler methods.[2,3,4]

Sodium oxalate: 2·5% solution.

Acetic acid: 1*M*.

Wash liquid: Ethyl alcohol.

Apparatus

The measurements were made by the derivatograph of Paulik, Paulik and Erdey.[5] We used a furnace that could be heated up to 1150°. The heating rate was controlled at 10° per min. The weights of precipitates used were about 400 mg.

Procedure

Neutralise 50–400 ml of solution containing 20–200 mg of calcium, 40–200 mg of strontium and 10–200 mg of barium to methyl orange, and add for each 100 ml 3 ml of 1*M* acetic acid. Boil the solution and add, dropwise, 2·5% sodium oxalate slowly in excess. (The solution should not contain ammonium salts because barium oxalate does not precipitate quantitatively in the presence of ammonium ions.) Let the precipitate stand overnight, and filter on a fine-porosity (G4) glass filter. Wash the precipitate first with several ml of cold water, then with 15 ml of ethyl alcohol, and finally dry by drawing air through the precipitate to constant weight. Weigh the dry precipitate. From the precipitate weigh a 0·2-g to 0·4-g aliquot accurately into the sample-holder crucible of the derivatograph. In calculating the results, the ratio of total precipitate weight: aliquot weight must be used as a multiplication factor. Use a 10°/min heating rate for the derivatographic measurement, and finish the procedure at 1140–1150°. From the developed derivatograms, results can be calculated on the basis of considerations described later.

DISCUSSION

In Fig. 1 a derivatogram obtained by the method is shown. The derivatograph marks the curves as a function of time. To achieve more comparable data, the derivatographic curves are re-drawn as a function of temperature. For simplicity

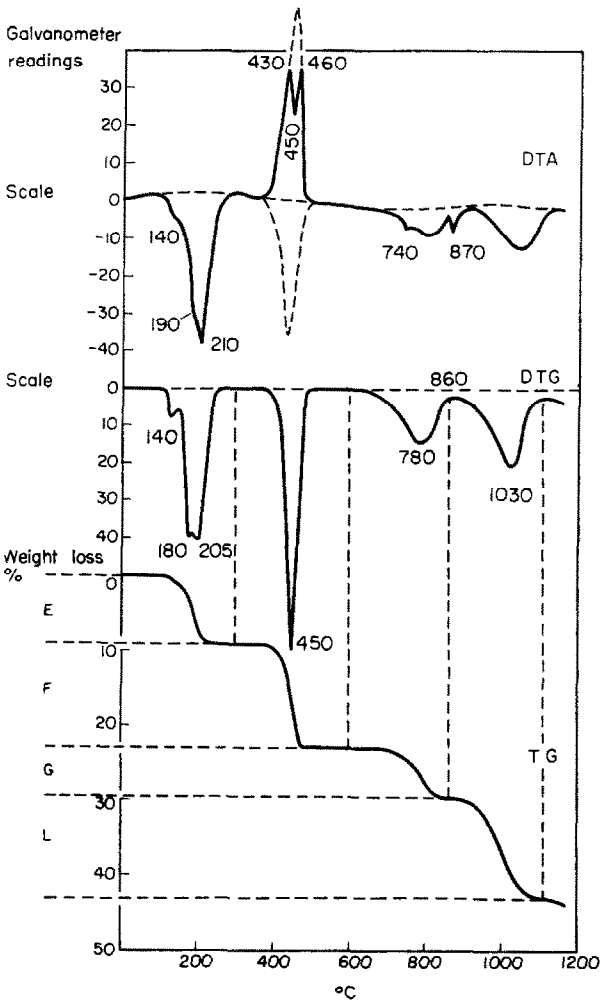


FIG. 1

the weights are calculated for 1 g of precipitate, although the precipitate weights used were about 0·2–0·4 g. Accurate calculation of the results can, of course, be made without any material alteration of the original derivatograms.

From the thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermoanalytical (DTA) curves, it can be seen that the decomposition processes are going on independently of one another. The precipitate showed no weight-losses up to 100°, *i.e.*, the air-dry precipitate contained no residual humidity. If, however, the precipitate contains moisture, the weight at 100° must be chosen as a

"precipitate weight". Between 100 and 250° the water of crystallisation of the precipitates is being lost. In acetic acid medium, calcium and strontium oxalates each precipitate with 1 mole of water of crystallisation, while barium oxalate has 0·5 mole water of crystallisation. According to the curves the oxalate hydrates lose their water content in the order barium, strontium, calcium. Under these experimental conditions, only barium oxalate hydrate is decomposed separately (at 140°), and decomposition of strontium and calcium oxalates took place at nearly identical temperatures; double peaks (180 and 205°) and inflexion points show that the two decomposition processes took place in quick succession.

After the loss of water, the anhydrous oxalates had constant weights between 250° and 360°. Then the decomposition of all three anhydrous oxalates took place at the same time. The rate of decomposition is maximal at 450°. Under other experimental circumstances, however, decomposition of the single oxalates can be obtained separately in the order calcium, strontium, barium, that is in the reverse order to the oxalate hydrates.[6]

At the decomposition of the oxalate hydrates there is an exothermal peak on the DTA curve. Although the processes $M(COO)_2 \rightarrow MCO_3 + CO$ are endothermal, carbon monoxide, formed in the decomposition, partly burns in the furnace area, yielding the exothermal peak. As a result of these two opposing processes, curves of various shapes can be gained, because these processes may be shifted in time.[7] The probable shapes of the two opposing curves are added in dotted lines to the DTA curve.

The three carbonates formed have constant weights between 500° and 620°, and first calcium carbonate, then strontium carbonate decomposes with loss of carbon dioxide, the oxides being formed. Decomposition of calcium carbonate begins at 620° and under these experimental circumstances is finished at 860°. Within this temperature range the decomposition of strontium carbonate begins, and is complete at 1100°. Decomposition of barium carbonate only begins above 1100°. At 740° and 870° on the DTA curve the endothermal recrystallisation processes of strontium and barium carbonates respectively are indicated. If carbon dioxide is removed from the furnace space by suction, the partial pressure of carbon dioxide decreases and the reactions take place at lower temperatures. The decomposition temperatures are also shifted towards lower values if a smaller heating rate is used. If for example the heating rate is 2°/min, strontium carbonate is completely decomposed at 1000°.

CALCULATION OF THE RESULTS

From the TG curve, in conjunction with the DTG minima, the following data can be obtained: weight of dry precipitate (at 100°), D, weight of removed water of crystallisation, E, weight of carbon monoxide formed in the decomposition of the oxalates, F, weight of carbon dioxide formed in the decomposition of calcium carbonate, G, and weight of carbon dioxide formed at the decomposition of strontium carbonate, L. From these data the amounts of calcium, C, strontium, S, and barium, B, can be calculated. Of the five values (D, E, F, G, L) only three are needed for the calculation of the three unknown values (C, S, B). The three values used for the calculation must be so chosen, that the error should be as small as possible. Of the values G and L must be used in every case, because from these calcium and strontium can be determined directly (i.e., the error of the result is equal to the error of the measurement). The

determination of barium however is made from three values, indirectly; the error of such measurements, as we have pointed out previously,[8] will be much greater than the errors of the individual measurements.

It is therefore necessary to choose one from among the D, E and F values. Errors were calculated using all possible combinations (G, L, D; G, L, E; G, L, F) as described previously.[1,8] It was assumed that the amounts of the single components were

TABLE 1

$$C = S = B = 1$$

$$\frac{\Delta D}{D} = \frac{\Delta E}{E} = \frac{\Delta F}{F} = \frac{\Delta G}{G} = \frac{\Delta L}{L} = 0{\cdot}1\,\%$$

Values used for calculation	$\frac{\Delta C}{C}$, %	$\frac{\Delta S}{S}$, %	$\frac{\Delta B}{B}$, %	total error, %
D, G, L	0·1	0·1	0·78	0·98
E, G, L	0·1	0·1	1·64	1·84
F, G, L	0·1	0·1	1·76	1·96

TABLE 2

	Taken, *mg*	Found, *mg*	Difference *mg*	Difference %
C	22·7	22·7	0·0	0·0
S	42·5	42·8	+0·3	+0·7
B	39·3	37·4	−1·9	−4·8
C	22·7	22·5	−0·2	−0·9
S	42·5	42·7	+0·2	+0·5
B	39·3	39·1	−0·2	−0·5
C	45·5	45·2	−0·3	−0·7
S	42·5	42·3	−0·2	−0·5
B	39·3	38·2	−1·1	−2·8
C	45·5	44·9	−0·6	−1·3
S	42·5	42·9	+0·4	+0·9
B	39·3	38·7	−0·6	−1·5
C	22·7	22·4	−0·3	−1·3
S	85·0	85·6	+0·6	+0·7
B	39·3	40·0	+0·7	+1·8
C	22·7	22·5	−0·2	−0·9
S	85·0	85·8	+0·8	+0·9
B	39·3	39·9	+0·6	+1·5
C	22·7	22·6	−0·1	−0·4
S	42·5	42·1	−0·4	−0·9
B	80·8	80·9	+0·1	+0·1
C	22·7	22·8	+0·1	+0·4
S	42·5	42·9	+0·4	+0·9
B	80·8	79·9	−0·9	−1·1

unity and equal ($C = S = B = 1$), and that the relative error of the single measurements were in all cases 0·1 % $\left(\frac{\Delta D}{D} = \frac{\Delta E}{E} = \frac{\Delta F}{F} = \frac{\Delta G}{G} = \frac{\Delta L}{L} = 0{\cdot}1\,\%\right)$. Since only comparable results were required, these assumptions could be justified. The errors $\frac{\Delta C}{C}, \frac{\Delta S}{S}, \frac{\Delta B}{B}$ obtained by the calculations are shown in Table I.

According to this, the least error occurs after calculations are made on the basis of the D, L, G values.

On the basis of simple stoichiometric considerations, the amounts of calcium, C, strontium, S, and barium, B, can be obtained from the precipitate weight, D, the weight of carbon dioxide formed in the decomposition of calcium carbonate, G, and the weight of carbon dioxide formed in the decomposition of strontium carbonate, L, by the following equations:

$$C = 0{,}91068 \,.\, G$$

$$S = 1{,}9911 \,.\, L$$

$$B = 0{,}58603 \,.\, D - 1{,}9457 \,.\, G - 2{,}5788 \,.\, L$$

The results are obtained in mg if the amounts of D, L and G are also in mg. The final results must be multiplied by the factor representing the ratio of total precipitate to the aliquot used.

The results of some determinations are shown in Table II.

Zusammenfassung—Zur Bestimmung von Ca, Sr und Ba in einer Probe muss man die Ionen zusammen als Oxalate fällen. Ein aliquoter Teil des Niederschlages wird in den Probetiegeln eines Derivatographen gewogen, der auf 1150°C heizbar ist. Ein Derivatogramm wird aufgenommen und aus ihm folgende Daten abgelesen: Gewicht des Niederschlages, Gewicht des Kohlendioxyds aus der Zersetzung des Calciumcarbonates und Gewicht des Kohlendioxydes aus der Zersetzung des Strontium carbonates. Mit diesen Daten können die Gehalte der drei Komponenten errechnet werden. Die Daten zur Berechnung wurden von 5 Bestimmungen genommen um eine Fehlerrechnung zu ermöglichen.

Résumé—Pour le dosage du calcium, du strontium et du baryum dans un échantillon, on les précipite ensemble sous forme d'hydrates et d'oxalates mixtes. Une partie aliquote du précipité doit être pesée dans le creuset support de l'échantillon; ce creuset fait partie d'un dérivatographe, ayant un four qui peut être chauffé à 1150°C. Une mesure dérivatographique est possible et les résultats suivants peuvent être obtenus d'après les courbes: poids du précipité, poids de l'anhydride carbonique formé par décomposition du carbonate de calcium et poids d'anhydride carbonique formé par décomposition du carbonate de strontium. D'après ces trois valeurs, les quantités de calcium, strontium et baryum dans l'échantillon peuvent être calculées. Les résultats, utilisés pour les calculs, sont choisis parmi cinq valeurs en se basant sur le calcul d'erreur.

REFERENCES

[1] L. Erdey, F. Paulik, G. Svehla and G. Liptay, *Z. analyt. Chem.*, 1961, **182**, 329.
[2] L. W. Winkler, *Z. angew. Chem.*, 1917, **30**, I, 302.
[3] *Idem. ibid.*, 1918, **31**, I, 80.
[4] *Idem, ibid.*, 187.
[5] F. Paulik, J. Paulik and L. Erdey, *Z. analyt. Chem.*, 1958, **160**, 241.
[6] L. Erdey and F. Paulik., *Acta Chim. Hung.*, 1955, **7**, 27.
[7] F. Paulik, J. Paulik and L. Erdey, *ibid.*, 1961, **26**, 143.
[8] L. Erdey and G. Svehla, *Z. analyt. Chem.*, 1960, **176**, 8.

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SEPARATION AND DETERMINATION OF CHROMIUM, TUNGSTEN, MOLYBDENUM AND VANADIUM BY PARTITION CHROMATOGRAPHY

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Summary—A method has been proposed for the separation and determination of microgram amounts of chromium, vanadium, tungsten and molybdenum, using the technique of partition chromatography. The solvent-mixture employed consisted of sym-collidine, 10 parts; iso-butanol, 38 parts, concentrated hydrochloric acid, 52 parts (v:v:v).

INTRODUCTION

VANADIUM of Group Vb of the Periodic Table, and chromium, tungsten and molybdenum of Group VIb show marked similarities in chemical properties and are, in the form of the metals, of considerable importance in alloy steels. In spite of their widespread use, however, methods for the separation and determination of microgram amounts of the four elements are not numerous. Several attempts have been made to separate mixtures of the elements by paper chromatography. Venturello and Ghe[1] used the radial paper chromatographic technique and a solvent-mixture composed of butanol, acetylacetic ester, and hydrochloric acid. Paper treated with perchlorate ion was employed by Murata[2] to separate the elements in the form of anions from each other and from sulphate ions. Aqueous solvents have also been used in an attempt to separate the elements,[3] but R_F values for chromate and molybdate are close, indicating overlap of the bands. Lacourt[4] obtained a more satisfactory separation by developing chromatograms with a mixture of acetone, chloroform and hydrochloric acid, after saturating the tank with the vapours of a mixture of equal parts of methylethylketone and chloroform. Many other solvent-mixtures have been tried, but in most cases there was either extensive tailing or the group of elements tended to migrate at the same rate.

This paper describes the investigations carried out and the results obtained with a solvent-mixture of the following composition: sym-collidine, 10 parts; iso-butanol, 38 parts; concentrated hydrochloric acid, 52 parts (v:v:v).

EXPERIMENTAL

Sym-collidine has been used in other circumstances as a constituent of solvent-mixtures in paper chromatography.[5] However, because of its high viscosity, it is necessary to dilute this solvent, if excessive periods of development are to be avoided. Because of its miscibility with alcohols, but low miscibility with water, a number of the former were examined and iso-butanol was ultimately selected. Because of the low basic strength of the anions, hydrochloric acid was chosen as a source of protons. To determine the optimal amount of collidine that should be present in the solvent-mixture, chromatograms were developed with solvent-mixtures containing varying proportion of collidine. The results are summarised in Table I.

It will be observed that satisfactory and consistent separations are achieved with solvent-mixtures containing 5 to 10% of sym-collidine. Further investigations indicated that the best combination was a solvent-mixture composed of 10 parts of sym-collidine, 38 parts of iso-butanol and 52 parts of concentrated hydrochloric acid.

Procedure

Solutions of sodium vanadate, molybdate, tungstate and chromate were prepared from AnalaR grade compounds, and mixtures containing varying proportions of the anions were obtained by mixing aliquots of these solutions. Using a micropipette, 0·01 ml of a mixture was applied to points 6 cm from the end of the strips of Whatman No. 1 filter paper, which were 40 cm long and 5 cm wide. The spots were allowed to dry in the air for 10 min, then the papers were transferred to a Shandon Chromatank previously saturated with the vapours of the developing agents (a beaker of solvent-mixture

TABLE I.—EFFECT OF COLLIDINE CONCENTRATION ON R_F VALUES

* Collidine content of solvent mixture, *volume* %	R_F values			
	Cr	V	W	Mo
0	0·65	0·54	0·65	0·65
1	0·34	0·39	0·52	0·52
2	0·32	0·48	0·66	0·80
4	0·29	0·35	0·64	0·77
5	0·29	0·39	0·68	0·79
10	0·28	0·37	0·68	0·81
30	0·92	0·85	0·65	0·65 (elongated)

* All the above solvent mixtures contained, in addition to collidine 38% of isobutanol, the remainder being concentrated hydrochloric acid.

was placed in the tank at least 1 hr before introducing the strips). After insertion of the papers, the solvent reservoir was filled with the solvent-mixture, the tank was closed, and the chromatogram was allowed to develop by the descending technique for a period of 24 hr. During this time the solvent front advanced approximately 30 cm.

After development, the strips were removed from the tank, and were allowed to hang in the air for 1 hr. They were then dried in an oven at 60°.

TABLE II.—DETECTION OF THE ELEMENTS

No.	Cr		V		W		Mo	
	μg	R_F	μg	R_F	μg	R_F	μg	R_F
1	32	0·30	22	0·40	17	0·70	8	0·83
2	32	0·28	44	0·38	11	0·69	40	0·80
3	32	0·28	4	0·38	28	0·68	20	0·84
4	6	0·29	8	0·40	55	0·69	20	0·83
5	—	—	—	—	28	0·69	20	0·84
6	—	—	22	0·38	28	0·70	20	0·84
7	16	0·28	—	—	28	0·68	20	0·82
8	16	0·30	22	0·40	28	0·71	20	0·84
9	96	0·37	4	0·45	17	0·71	8	0·82
10	6	0·28	8	0·37	110	0·69	80	0·80
11	6	0·28	44	0·38	17	0·71	8	0·81

Detection of the elements

The components of the mixture were located by spraying the dry chromatogram with suitable detecting agents. One strip was sprayed with a mixture of 5% pyrogallol in alcohol and was then dried. The elements, if present, produce four bands as follows: green (Cr), blue (V), light brown (W), and bluish (Mo). A second strip was sprayed with 1% 8-hydroxyquinoline solution in a mixture of sodium acetate, acetic acid and water. With this reagent the elements produce bands which are yellow, excepting that of vanadium, which has a greenish tinge.

The R_F values were calculated for each ion, and the results are summarised in Table II.

It will be observed from the Table that less than 10 μg of each element can be separated from much higher concentrations of other elements and detected. It will also be observed that the R_F value of a particular species is only slightly influenced by the concentration of the other species present.

Determination of the elements

For the determination of the four elements, the procedure described above was used for separation, except that Whatman No. 40 paper was substituted for Whatman No. 1 paper. The former is acid washed paper, and was found to yield more compact bands after development.

To carry out the determination, four chromatograms of the same mixture were prepared in the same tank simultaneously. After drying, one of the chromatograms was sprayed with pyrogallol and other with 8-hydroxyquinoline reagent. By this means the bands of the individual components of the mixture were located. By comparison the position of the elements on the untreated chromatograms were located. A 3-cm square was cut around the region of the detected element. The paper removed in this way was boiled with 10 ml of 1*N* hydrochloric acid for 15 min to extract the metal ion. The extract was cooled, filtered and used for the determination of the element using the appropriate procedure, as indicated below.

(*a*) *Chromium:* The acid extract was carefully evaporated to dryness, and the residue was dissolved in water. By boiling with excess sodium peroxide until the excess was destroyed, all the chromium was oxidised to the sexavalent state. The quantity of chromium present was then determined photometrically using the diphenylcarbazide method.[6] Measurements were made at 540 mμ, and the chromium content was evaluated from a calibration curve.

(*b*) *Vanadium:* The hydrochloric acid extract was made alkaline with sodium hydroxide and was then boiled with sodium peroxide, to oxidise vanadium to the quinquevalent state. The solution was filtered into a 50-ml volumetric flask, and 5 ml of 4*N* H_2SO_4, 1 ml of 1:1 phosphoric acid and 0·5 ml of 0·6*M* sodium tungstate were added. The mixture was shaken until the yellow colour of phosphotungstovanadic acid was formed. The solution was now boiled, cooled and made up to a standard volume. The extinction was measured at 400 mμ, and the vanadium content was determined from a calibration graph.

(*c*) *Tungsten:* The hydrochloric acid extract was transferred to a separating funnel together with 1 ml of 1*N* NaOH, 6 ml of 5% KCNS solution, and 10 ml of 10% $SnCl_2$ in concentrated hydrochloric acid. The solution was well shaken after the addition of each reagent. The mixture was allowed to stand for 1 hr, to permit the full development of the yellow colour. The thiocyanate complex was then extracted with two 10-ml portions of ethyl ether which had previously been shaken with potassium thiocyanate and stannous chloride solution.

The ether extract was transferred to a 25-ml volumetric flask and was diluted to standard volume with ether. The extinction of the solution was measured at 420 mμ,[6] and the tungsten content was determined by reference to a calibration curve similarly prepared.

(*d*) *Molybdenum:* The hydrochloric acid extract was transferred to a separating funnel, and 6 ml of 5% KCNS and 2 ml of 10% $SnCl_2$ in concentrated hydrochloric acid were added. After shaking, the amber-red colour formed was extracted into ether, as for tungsten. The extinction of this solution at 475 mμ[6] was measured, and the amount of molybdenum present was obtained by reference to a calibration graph.

Blanks were used in all the colorimetric determinations.

TABLE III.—ANALYSIS OF MIXTURES

Cr		Mo		W		V	
Given	Found	Given	Found	Given	Found	Given	Found
9	8·5	—	—	—	—	90	71
10	9	12	20	50	42	10	10
—	—	17	17	40	26	42	20
90	80	10	9	5	4·5	—	—
85	80	—	—	10	9	10	10

RESULTS

As a check on the procedure, a number of "unknown" mixtures were analysed by one of us (A. S. W.). The results are summarised in Table III. (All quantities in the Table are in micrograms.)

It will be observed from Table III that complete recovery of the individual elements was achieved in only three cases. In the others, recovery was 90% or more. In view of the small amount of material present, these results can be considered to be very satisfactory.

The low results may in part result from the following causes: firstly, the element may not be completely located in the "detected "spot on the chromatogram because of slight tailing from the starting point; secondly, extraction of the element from the paper may not have been complete; thirdly, there may have been errors or losses in the final evaluation stage of the analysis.

DISCUSSION

The use of an acid solvent-mixture for the paper separation of this group of anions requires a little explanation. The metals were placed on the paper in the form of their sodium salts, chromate, vanadate, tungstate and molybdate. The aqueous phase therefore contained the anions of group Vb and group VIb metals plus sodium ions, and hydroxonium ions are introduced by the mobile solvent. Under these conditions equilibria similar to the following arise:

$$4H^+ + CrO_4^{=} \rightleftharpoons 2H_2CrO_4 \rightleftharpoons H_2O + Cr_2O_7^{=}$$

Sym-collidine may also react with the acid introduced into the solvent, and become protonated at the basic nitrogen

$$\text{Collidine} + H^+ \rightleftharpoons [\text{Coll. H}]^+$$

The position of equilibrium in these reactions will be dependent on the acidity of the solvent mixture, since the concentration of hydrogen ions available in the aqueous phase will be controlled by partition of these ions from the mobile organic phase back into the water phase. Increasing the collidine content of the developing agent might therefore have several effects: (i) The increased concentration of protonated material can attract (by ion association) a larger proportion of anions into the mobile phase. This effect was exhibited by molybdenum (Table I); (*ii*) dissociation of protonated collidine can increase the acidity of the aqueous phase resulting in increased association in this phase and less solution in the mobile solvent. This effect was shown by chromium and vanadium; (*iii*) this reduced movement could be caused by partial reduction of these elements by the paper and chloride ions, since a large excess of collidine (*e.g.* 30%) resulted in enhanced movement (greater solution in the organic phase) of these two elements. The movement of tungstate did not appear to be significantly influenced by the presence of collidine in the solvent.

The complexity of the species that may be derived from the four elements studied in aqueous solution (*e.g.*, poly-salts) makes a complete explanation impossible, but in general terms, the separation of the anions can be explained by a mechanism based on the association of the anions with protonated collidine. The butanol in the solvent acts merely as a diluent for the collidine, and accelerates the rate of development of the chromatogram by reducing the viscosity of the solvent mixture.

Zusammenfassung—Eine verteilungschromatographische Methode zur Trennung und Bestimmung von Mikrogrammengen von Chrom, Vanadin, Wolfram und Molybdän wird vorgeschlagen. Die verwendete Lösungsmittelmischung ist sym.-Collidine:Isobutylalkohol:conc. Salzsäure = 10:38:52 (volumsteile).

Résumé—Les auteurs proposent une méthode de séparation et de dosage de microgrammes de chrome, vanadium, tungstène et molybdène, par chromatographie de partage. Le mélange de solvants utilisé comprend: 10 parties en volumes de collidine symmétrique, 38 parties d'isobutanol et 52 parties d'acide chlorhydrique concentré.

REFERENCES

[1] Giovani Venturello and Anna Maria Ghe, *Ann. Chim.* (*Rome*), 1957, **44**, 960.
[2] Akira Murata, *Nippon Kagaku Zasshi*, 1957, **78**, 395; *Chem. Abs.*, 1958, **52**, 7006*e*.
[3] E. Blucher and M. Lederer, *J. Chromatography*, 1960, **3**, 290.
[4] Alice Lacourt, *Proceedings of the International Symposium of Microchemistry*, Birmingham, England, Pergamon Press, Ltd., London, 1958, p. 439.
[5] James B. Headridge and Robert J. Magee, *Talanta*, 1958, **1**, 117.
[6] E. B. Sandell, *Colorimetric determination of traces of metals*. Interscience, New York, first edition, 1944. pp. 191, 440, 429, 333.

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STEPWISE DETERMINATION OF CADMIUM, MERCURY AND TELLURIUM

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Summary—Methods for the analysis of the tellurides of cadmium and mercury are described and discussed. In analysing mixtures of the two tellurides, cadmium and mercury can be determined by two stepwise EDTA titrations and tellurium is then determined by difference. Alternatively, tellurium and mercury can be directly determined gravimetrically in the presence of EDTA as tellurium dioxide and mercury-Bismuthiol II. For analysing small quantities, both cadmium and mercury are determined photometrically by dithizone methods at different acidities, and tellurium is determined photometrically by the Bismuthiol II method. The three elements may be determined in one solution, so that accurate results may be obtained on a small amount of sample. The methods are simple and rapid.

INTRODUCTION

FOR analysing either cadmium telluride or mercury telluride a similar method to that used for analysing lead telluride can be employed, *viz.* the tellurium is determined gravimetrically and the lead titrated complexometrically.[1] This method cannot, however, be directly applied to the analysis of mixtures of tellurides. Also, a limited sample size can often create an analytical problem because it requires the use of sensitive methods for the determination of the separate elements. The present paper reports methods suitable for determining cadmium, mercury and tellurium, both in limited and unlimited sample sizes; the analysis of three elements in one solution makes their determination possible for a minimum amount of sample. For unlimited samples cadmium and mercury are titrated together complexometrically; then, after precipitating the mercury from this solution as its Bismuthiol II complex,[2] mercury may be directly determined by weighing the precipitate or by titrating the EDTA liberated from the mercury-EDTA complex. Cadmium is obtained by difference. Tellurium is determined gravimetrically as tellurium dioxide,[1] or obtained by difference between the amount of sample taken and the sum of both mercury and cadmium found. For limited samples both cadmium and mercury are determined photometrically with dithizone[3] at different acidities, and tellurium is determined by the Bismuthiol II method.[4] The dithizone methods for cadmium and mercury are well known; however, without the two recently developed methods for tellurium the analysis of the tellurium mixture would not be easy, especially if the supply of sample is limited.

EXPERIMENTAL

Reagents

0·025*M EDTA solution;* Prepared from disodium ethylenediaminetetra-acetic acid and standardised by an appropriate method.

0·025*M standard zinc solution:* Prepared from pure zinc metal and hydrochloric acid.

Erio T indicator solution: Grind to a fine powder, 0·1 g of Eriochrome Black T with 10 g of sodium chloride.

pH 10 *buffer solution:* Dissolve 70 g of ammonium chloride in 570 ml of ammonium hydroxide (sp. gr. 0·9) and dilute to 1 litre with water.

Bismuthiol II solution: A 1% aqueous solution of the potassium salt of mercaptophenylthiolthiadiazolone.

Standard cadmium solution: Dissolve 0·5000 g of pure cadmium in 10 ml of nitric acid (1:1) and dilute to 500 ml with water. Prepare a solution containing 1·0 μg of cadmium per ml by appropriate dilution.

Standard mercury solution: Dissolve 0·1354 g of mercury II chloride in 100 ml of 1*N* sulphuric acid (1 mg of mercury per ml). Prepare a solution containing 2·0 μg of mercury per ml by appropriate dilution.

Standard tellurium solution: Dissolve 0·1 g of pure tellurium in 5 ml of concentrated sulphuric acid by heating. Fume to evaporate off most of the acid. After cooling, carefully add 100 ml of water and dissolve the tellurous acid precipitate by adding a minimum amount of 4*M* potassium hydroxide solution, making to 1 litre. This solution contains 0·1 mg of tellurium per ml. Prepare a solution containing 5 μg of tellurium per ml by appropriate dilution.

Citric acid: 1*M*.

Ammonium sulphate solution: A 50% w/v aqueous solution adjusted to pH 2·2 with sulphuric acid.

Sulphuric acid: 5*N*.

Dithizone solution: A 0·01% w/v solution in chloroform. Store in a refrigerator. Prepare a fresh solution of 0·001% in chloroform from the stock solution every day.

Sodium hydroxide solution: A 50% solution obtained from J. T. Baker Chemical Company.

Apparatus

Beckman spectrophotometer Model DU and Beckman pH meter Model G or equivalent were used. Other chemicals used were reagent grade.

Procedures

1. *Dissolution of sample*

A. *For unlimited samples.* Weigh 0·1 g or more of sample into a 250-ml beaker. Add 2 ml of concentrated nitric acid and 1 ml of concentrated hydrochloric acid. If necessary, heat gently on a hot plate to speed up the reaction until solution is complete.

B. *For limited samples.* Add 1 ml of concentrated nitric acid and 1 or 2 drops of concentrated hydrochloric acid.

2. *Analysis of solution* 1-*A*

A. *Tellurium.* Add accurately a slight excess of EDTA and dilute to approximately 50 ml with water. Adjust to pH 10 with ammonium hydroxide solution. The solution should be clear and colourless. Add Erio T indicator (approximately 80 mg) and back titrate the excess EDTA with the standard zinc solution, the end-point being from blue to purplish red. This titration gives the sum of the cadmium and mercury contents, and the tellurium content is obtained by difference. If its direct determination is desired, readjust the pH to 4·5 with hydrochloric acid to precipitate tellurous acid. Cover the beaker with a watch glass, boil, cool to room temperature or below, and filter through a sintered glass crucible. Wash three times with a few-ml portions of 50% methanol. Dry at 132° to 140° until constant weight is obtained. Weigh as TeO_2, the gravimetric factor being 0·7995.

B. *Mercury.* Heat the filtrate from the tellurium determination to boiling and make ammoniacal; add a slight excess of Bismuthiol II and stir to precipitate the mercury complex. While hot, filter the solution through a sintered glass crucible. Wash three times with water. (If the gravimetric determination of mercury is desired, dry the precipitate at 105° until constant weight is obtained; the gravimetric factor is 0·3080.) To the filtrate add 5 ml of the pH 10 buffer solution, (Erio T indicator powder, if necessary) and back titrate the EDTA liberated from the mercury-EDTA complex with the standard zinc solution. This titration is for mercury. The titrimetric result may be compared with the gravimetric one.

C. *Cadmium.* The difference in the two EDTA titrations is for cadmium.

3. *Analysis of solution* 1-*B*

The solution is made to a suitable volume, 50 or 100 ml.

A. *Mercury.* To an aliquot containing not more than 20 μg of mercury, add suitable amounts of 5*N* sulphuric acid and water so that the final volume is approximately 25 ml and contains 25 milliequivalents of sulphuric acid. Add 10 ml of 0·001% dithizone in chloroform and shake vigorously for 1 min. Filter the extract through glass wool and measure the absorbance at 500 mμ against a reagent blank. Prepare similarly a calibration curve with known amounts (less than 20 μg) of mercury.

B. *Cadmium.* After the mercury determination, drain off practically all of the organic phase. Shake the aqueous phase with a few ml of chloroform to remove any dithizone remaining. Drain off the chloroform as completely as possible and discard it. Add 2 ml of 50% sodium hydroxide solution

to raise the pH >12, and 4 drops of 20% hydroxylamine hydrochloride solution. Cool and extract for 1 min with 10 ml of 0·001% dithizone in chloroform (5 ml may be used if the amount of cadmium in the solution is less than 2 μg). Filter the extract through glass wool and measure the absorbance at 530 mμ against a reagent blank. Prepare similarly a calibration curve with known amounts (less than 10 μg) of cadmium.

C. *Tellurium.* After the cadmium determination, drain off practically all of the organic layer. Acidify the aqueous layer and remove any dithizone by extracting with chloroform. Separate the aqueous phase and adjust to pH 2·2 after adding 1 ml of 0·025*M* EDTA solution, 1 ml of 1*M* citric acid solution, and 6 ml of 50% ammonium sulphate solution. Add 3 ml of 1% Bismuthiol II solution and let stand for 20 min or longer. Again adjust to pH 6·5, transfer to a 125-ml separatory funnel, and extract with 10 ml of carbon tetrachloride for 1 min. Filter the extract through glass wool and measure the absorbance at 335 mμ against a reagent blank. Prepare similarly a calibration curve with known amounts (less than 50 μg) of tellurium.

DISCUSSION AND RESULTS

Since the tellurides are usually made of pure metals, it may be reasonably assumed that the samples contain negligible amounts of impurities. Cadmium telluride was easily decomposed in hot concentrated nitric acid but not in sulphuric acid; mercury telluride could be decomposed in hot sulphuric acid but not easily in nitric acid. An attempt was made to decompose the sample of tellurides of cadmium and mercury with concentrated nitric acid first and concentrated sulphuric acid later; incomplete decomposition resulted. This difficulty is overcome by the use of nitric acid and hydrochloric acid. After complete decomposition the solution, which is made ammoniacal in the presence of EDTA, should be colourless and clear. If the solution becomes dirty brown and turbid, this indicates incomplete decomposition. When chloride was present, mercury was lost upon fuming with sulphuric acid; however, no loss of mercury was noticed when the sample was heated with the mixture of nitric acid and hydrochloric acid at a temperature below 150°. Therefore, the mixture of nitric acid and hydrochloric acid seems to be the best for the decomposition of the sample; gentle heating may be necessary to speed up the reaction.

For analysing either cadmium telluride or mercury telluride, the methods for analysing lead telluride may be directly applied. For analysing a mixture of cadmium telluride and mercury telluride, other methods than the one discussed herein may be feasible for determining cadmium and mercury individually. For example, after separating tellurium as tellurous acid in the presence of EDTA, the combined amount of cadmium and mercury might be found by back titration of the filtrate with a standard magnesium solution. Then a slight excess of cyanide might be added to complex both mercury and cadmium, followed by the addition of formaldehyde to decompose free cyanide and the relatively weak cadmium cyanide complex. A further EDTA titration should give the amount of cadmium. The difference between the combined amount of cadmium and mercury and the amount of cadmium should give the amount of mercury.

When the values of cadmium and mercury are known through two stepwise EDTA titrations, tellurium may be determined by difference. A slightly higher result for mercury was often obtained by the gravimetric method for more than 100 mg of mercury. This may be attributed to the fact that a very small amount of water trapped in the large compact precipitate may be difficultly removed at 105°. Therefore, the EDTA titration is usually preferred. However, the gravimetric results may be used for comparison.

The proposed procedure is simple and accurate (see Table I). All three elements

can be determined in one solution. By using EDTA as a masking agent, tellurium is precipitated in the presence of mercury and cadmium, then mercury is precipitated in the presence of cadmium by Bismuthiol II.[2] An examination of the precipitates of tellurium dioxide and of mercury-Bismuthiol II showed that they contained only traces of impurities.

For analysing limited samples of the telluride mixture, the dithizone methods are selective for cadmium and mercury.[3] It is known that mercury can be extracted by

TABLE I. GRAVIMETRIC AND TITRIMETRIC DETERMINATION OF CADMIUM, MERCURY AND TELLURIUM.

Element taken, *mmole*	Form	Found, *mmole*
0·178 Cd	Cd	0·179[b]
0·245 Hg	HgO	0·245[a]
0·470 Te	Te	0·469[c]
0·153 Cd	CdTe	0·150
0·153 Te	CdTe	0·151
0·416 Cd	CdTe	0·413
0·416 Te	CdTe	0·416
0·313 Hg	HgTe	0·318[a]
0·313 Te	HgTe	0·310
0·304 Hg	HgTe	0·302[b]
0·304 Te	HgTe	0·301
0·153 Cd	CdTe + HgTe	0·150[b]
0·313 Hg	CdTe + HgTe	0·316[a]
0·466 Te	CdTe + HgTe	0·461
0·125 Cd	CdTe + HgTe	0·124[b]
0·250 Hg	CdTe + HgTe	0·250[a]
0·375 Te	CdTe + HgTe	0·371

[a] By Bismuthiol II method[2]
[b] By EDTA titration[1]
[c] By gravimetric method as TeO_2[1]

TABLE II. PHOTOMETRIC DETERMINATION OF CADMIUM, MERCURY AND TELLURIUM.

Element taken, *μg*	Found, *μg*
8·0 Hg + 500 Cd	8·1 Hg
8·0 Hg + 500 Te	8·0 Hg
8·0 Hg + 500 Cd + 500 Te	8·0 Hg
2·0 Cd + 40 Hg	2·0 Cd[a]
2·0 Cd + 200 Te	2·0 Cd
2·0 Cd + 40 Hg + 200 Te	2·0 Cd[a]
30 Te + 5 Cd	30·1 Te
30 Te + 20 Hg	30·0 Te[a]
30 Te + 5 Cd + 20 Hg	30·0 Te[b]
20 Te + 10 Cd + 20 Hg	25·5 Te[c]
30 Te + 10 Cd + 20 Hg	29·8 Te[d]

[a] Mercury was removed by dithizone in 1*N* sulphuric acid.
[b] Both mercury and cadmium were removed by dithizone.
[c] Only mercury was removed, no EDTA was added.
[d] Only mercury was removed and 0·1 mmole of EDTA was added.

dithizone in the presence of many metals, including cadmium. It has been reported that tellurium is also extracted by dithizone at pH 1 and in 1*N* hydrochloric acid medium.[5] However, it was found that no noticeable tellurium was extracted in 1*N* sulphuric acid, as demonstrated in Table II. The dithizone extraction of cadmium at pH > 12 is selective; mercury is previously removed, and tellurium is not extractable by dithizone in an alkaline medium. Although the addition of cyanide makes the dithizone extraction for cadmium more selective, it may not be necessary for the pure materials studied. If the presence of significant amounts of interfering metals, *e.g.*, copper, is known, cyanide must be used. The subsequent tellurium determination with Bismuthiol II should be made after the cyanide has been removed either by vaporisation from the acid medium or by decomposition with formaldehyde. Alternatively, tellurium may be determined on a separate aliquot after removing mercury, if sufficient sample is available. By using EDTA as a masking agent, it was found that small amounts of cadmium did not affect the tellurium determination. Cheng's Bismuthiol II method for tellurium is the most sensitive chemical method known at present and should not be confused with other less sensitive methods employing the same reagent; for details the original paper should be consulted.[4] Nitrite and other oxidising agents interfere with the determination of tellurium with Bismuthiol II; therefore, any brown fumes formed during the dissolution of the sample with hydrochloric acid and nitric acid should be removed. If their presence is suspected, the solution may be evaporated to sulphuric acid fumes after separating the mercury and cadmium and then followed by the Bismuthiol II method for tellurium.

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Zusammenfassung—Methoden zur Analyse der Telluride von Cadmium und Quecksilber werden diskutiert. Cadmium und Quecksilber können stufenweise mit ÄDTE titriert werden und das Tellur wird aus der Differenz (Gewicht des Ausgangsmaterials) erhalten. Oder aber Tellur und Quecksilber können direkt gravimetrisch als TeO_2 in Gegenwart von ÄDTE und Quecksilber mit Bismuthiol II bestimmt werden. In kleinen Proben werden Cadmium und Quecksilber bei verschiedener Azidität nach der Dithizonmethode und Tellur mittels Bismuthiol II photometrisch bestimmt. Die drei Elemente können in einer Probelösung bestimmt werden, sodass genaue Ergebnisse auch bei kleinen Probemengen erhalten werden. Die Methoden sind rasch und einfach.

Résumé—L'auteur décrit et discute les méthodes d'analyse des tellurures de cadmium et de mercure. En analysant le produit de départ des mélanges des deux tellurures, le cadmium et le mercure peuvent être dosés par deux titrages successifs au moyen de l'EDTA et le tellure est ensuite déterminé par différence.

Le tellure et le mercure peuvent être dosés directement par gravimétrie en présence d'EDTA sous forme de TeO_2 et de bismuthiol II de mercure. Pour l'analyse de faibles quantités, le cadmium et le mercure sont dosés tous les deux par photométrie par les méthodes à la dithizone à différentes acidités, le tellure est titré par photométrie par la méthode au bismuthiol II. Les trois éléments peuvent être dosés sur une solution, de sorte que l'on peut obtenir des résultats précis sur une faible quantité d'échantillon. Les méthodes sont simples et rapides.

REFERENCES

[1] K. L. Cheng, *Analyt. Chem.*, 1961, **33**, 761.
[2] V. Sedivec, *Coll. Chem. Czech. Comm.*, 1951, **16**, 398.
[3] E. B. Sandell, *Colorimetric Determination of Traces of Metals*. Interscience Publishers, New York, 3rd Ed., 1959.
[4] K. L. Cheng, *Talanta*, 1961, **8**, 301.
[5] S. Hikime, *Bull. Chem. Soc. Japan*, 1956, **29**, 842.

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THE APPLICATION OF AN IMPROVED STEAM DISTILLATION APPARATUS TO THE DETERMINATION OF FLUORIDE IN ROCKS AND MINERALS*

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Summary—The efficiency of the Willard and Winter steam distillation of fluoride can be improved by using sulphuric or phosphoric acid instead of perchloric acid solutions. However, sulphate and phosphate must be kept out of the distillate, for they interfere in many methods of determination, including the commonly-used thorium nitrate titration.

A newly-designed apparatus is described which permits close control of the distillation, and rapid and complete recovery of fluorine, free from significant amounts of sulphate or phosphate. Procedures are outlined whereby fluorine can be quantitatively recovered from silicate rocks and minerals and easily determined with precision and accuracy.

FLUORINE determinations are mostly accomplished after steam distillation according to Willard and Winter.[21] In silicate analysis, preliminary operations normally include an alkaline fusion followed by a Berzelius separation or some modification of it.[8] After steam distillation from acid solution, fluoride in the distillate is determined by one of a number of methods.[19]

The fusion and separation operation has been much simplified as a result of the work of Shell and Craig,[15] and of Grimaldi, Ingram, and Cuttitta,[6] who use a zinc oxide-sodium carbonate flux. Leaching of the melt with water results in the separation of fluorine from most of the silica and alumina in a single operation.

For the determination of fluorine in the distillate, thorium nitrate titration in 50% ethanol was used in this work because in our experience it is reliable and precise. The details of the procedure are due to Ellestad,[4] and are based on the work of Willard and Winter,[21] Hoskins and Ferris,[10] Armstrong,[1] and others. In this titration, phosphate must be absent, and sulphate in excess of about 0·5 mg cannot be tolerated. Undoubtedly other methods of determination are equally satisfactory. Xylenol Orange may prove an excellent reagent for fluorine.[20]

Since steam distillation was first proposed as a key step in the determination of fluorine in silicates, considerable attention has been given to the design of stills in attempts to reduce the time and supervision required,[5,11,12,14] prevent entrainment of the distilling acid,[13] and achieve quantitative recovery of the fluorine.[10] To date, spray traps,[17,18] special steam outlet tubes,[16] and control of distillation rate[9,11] have not been entirely successful. That incomplete recovery of fluorine remains a problem has been confirmed recently by Haff, Butler and Bisso.[7] A valuable study of factors involved in steam distillation of fluorine has been carried out by Dahle and Wichmann,[3] and the whole problem of determining small amounts of fluorine has been exhaustively reviewed by Valach.[19]

To minimise acid entrainment and improve fluorine recovery, a special still has

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been designed (Fig. 1). The essential feature of this apparatus is an internal splash trap which removes entrained acid from the steam without permitting condensation. The distillation from sulphuric acid solution containing a little perchloric acid normally requires about 1 hour, including the time required to bring the sample solution up to distilling temperature. Heating is done by means of a manually controlled flame, but may also be accomplished automatically.[5,12,14]

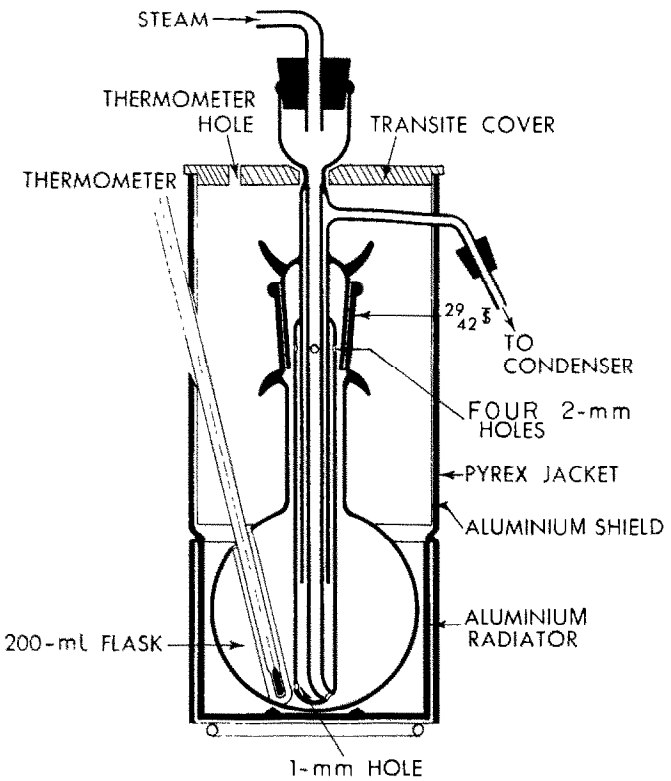


FIG. 1.—Special still for the steam distillation of fluorine.
Steam is generated in a 2000-ml flask by boiling water containing a little sodium hydroxide. A 200-mm coil type Graham condenser is convenient for use with this still.

An air bath consisting of a Pyrex jacket lined with bright aluminium sheet completely encloses the still. A window should be cut in the aluminium for observation purposes.

In operation, steam passes through the sample solution, rises between the neck of the flask and the trap, enters the latter through four 2-mm diameter holes within the 29/42$ stopper, passes downwards to the exit tube which surrounds the steam inlet, and then upwards to the outlet. A 1-mm hole which drains the trap should be located 90° from the thermometer well, rather than immediately opposite it as schematically indicated in the drawing: this avoids erratic thermometer readings.

The steam inlet should dip just below the surface of 30 ml of distilling acid, and the steam exit tube should reach within about 1·5 cm of the surface of the solution at its highest level—*i.e.*, before the distillation is started. If 30 ml of distilling acid are used,

and the sample solution and washings do not exceed 25 ml, the end of the steam exit can be as low as the centre of the 200-ml flask. If too much liquid is used, some of it will, of course, be thrown over into the condenser as soon as distillation starts.

A cross-section of the flask and trap at the level of the four 2-mm holes (Fig. 2) gives the recommended tubing dimensions.

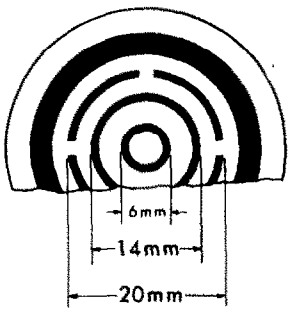


FIG. 2.—Cross section of still at the level of the four 2-mm holes which admit steam to the internal splash trap, showing the recommended tubing dimensions.

In setting up the still, it is advantageous to bolt the cast aluminium radiator to a supporting ring. The air bath may then be supported on the radiator by means of an annular constriction.

The entire still is made of Pyrex glass.

Perchloric acid was employed by Willard and Winter in their original procedure,[21] and has the advantage that moderate concentrations in the distillate are without sensible effect on the thorium nitrate titration. However, distillation of fluorine from perchloric acid is not as effective as from sulphuric or phosphoric acid,[3] because a lower temperature must be used. With the new still, it is possible to take full advantage of the higher temperatures attainable with sulphuric or phosphoric acids, without collecting harmful amounts in the distillate.

Recovery of fluorine from sulphuric acid solution is much improved if a little perchloric acid is also present. Some of this distils with the fluorine and presumably helps to prevent absorption on the glass surfaces within the still. In the recommended procedure, a small perchloric acid addition is made during the preparation of the solution. This addition improves the separation of alumina, and is conveniently used to rinse the fusion crucible, which may otherwise retain a little fluorine.

Shell and Craig[15] have pointed out that reasonably good results for fluorine in silicates can often be obtained without any separations before distillation from perchloric acid solution. In their rapid procedure, the sample is simply fused with sodium carbonate, transferred to the distilling flask with water, and distilled after the addition of perchloric acid. For phosphate rock, this is in fact the preferred procedure, since phosphate prevents complete recovery of fluorine in water leaching of alkali carbonate fusions.

To investigate the possibilities of direct distillation, 0·1 g and 0·2 g of several silicate samples were decomposed by sodium peroxide fusion and distilled directly with sulphuric or phosphoric acids. Experiments with sulphuric acid were not very successful because of the separation of large amounts of gelatinous silicic acid. With phosphoric acid, on the other hand, no difficulties were encountered: the water leach of the

peroxide fusion dissolved almost completely, and relatively little silicic acid separated during distillation. The new still proved almost completely effective in preventing the collection of phosphate in the distillate, even when the distilling temperature was increased to 160°. A rapid procedure involving direct distillation from phosphoric acid after sodium peroxide fusion is presented, but should be used with caution: undoubtedly it cannot be used, for example, with samples containing much sulphur, unless a method of determination is available which is unaffected by sulphate.

The longer method given, involving mixed alkali carbonate-zinc oxide fusion and separation of silica and alumina before distillation, is quite generally applicable to silicate rocks and minerals.

EXPERIMENTAL

Reagents

Special flux: Grind together and mix thoroughly zinc oxide and anhydrous alkali carbonates in the ratio K_2CO_3:Na_2CO_3:ZnO::9:7:3 (parts by weight). Run a blank determination to be sure that the flux does not contain fluorine.

Monochloracetate buffer: Dissolve 9·5 g of monochloracetic acid in water. Neutralise half the solution with carbonate-free sodium hydroxide, using phenolphthalein indicator. Combine and dilute to 50 ml. The buffer should be freshly prepared.

Alizarin Red S indicator: 0·05% aqueous solution.

Standard thorium nitrate: 0·005*M* in 0·04% nitric acid.

Standard fluoride solution: Heat reagent-grade sodium fluoride in a platinum crucible at low red heat (650°) for 1–2 hr. Cool, weigh exactly 0·1500 g, dissolve in water, and dilute to 200 ml. One ml of this solution contains 0·000339 g of fluoride, and is very approximately equivalent to 1 ml of the standard thorium nitrate solution (theoretically 1 ml of 0·005*M* $Th(NO_3)_4$ = 0·000380 g of F).

Procedure for silicate rocks and minerals

Grind somewhat more than 0·5 g of sample to an impalpable powder in an agate mortar, weigh 0·5000 g into a large (60-ml) nickel crucible, and add 6 g of special flux. Mix throughly, and heat, tightly covered, at the maximum temperature of a Meker burner for 35 min. Only the bottom half of the crucible should become heated to redness during the fusion. The crucible cover may be cooled by means of another containing water,[9] to be certain that there is no loss of fluorine.

Cool, add about 25 ml of water, and keep warm overnight. Because creeping sometimes occurs, the crucible should be placed on a clean cover glass and protected from the laboratory atmosphere, which may contain fluoride.

Transfer the contents of the crucible quantitatively to a 250-ml beaker, using about 80 ml of water. Rinse the crucible briefly with 10 ml of 1:10 perchloric acid, and pour this all at once into the beaker. Boil for 5 min, and filter into a 300-ml platinum or silver dish. Wash once or twice with hot water, sluice the residue back into the beaker, reboil and refilter. Wash with hot water, ignoring any peptisation which may occur.

Evaporate the filtrate (in silver or platinum, not in glass) to near dryness on the steam bath, and transfer to the special still through the steam inlet tube, using a minimum of water. Add about 20 mg of potters' flint. Put 30 ml of 24*N* sulphuric acid in the silver dish, and add it cautiously to the sample solution, dropwise at first to avoid mechanical loss. The liquid level in the still must be kept at least 1–1·5 cm below the end of the steam outlet in the splash trap.

Stopper the steam inlet, and heat until the thermometer indicates a temperature of about 130°. Do not place the receiver under the condenser until the first signs of condensate appear in the exit tube of the still: otherwise, carbon dioxide collected therein will require excessive additions of alkali, which is undesirable. If there is any indication that some of the solution may have splashed over into the condenser, the first fraction should be returned to the still through the steam inlet, and redistilled.

Steam distil at a rate of about 2–3 ml per min, holding the temperature at a predetermined optimum (see below). Collect about 100 ml of distillate after this temperature has been reached. If the fluorine content of the sample is at all likely to be high—above 0·5–1·0%—a further 100 ml should be collected and treated separately. With most rocks, no fluorine will be found in the second 100 ml. With fluorine bearing minerals (*e.g.*, lepidolite), 300–500 ml should be collected, and the last 100 ml should be treated separately to provide assurance that the distillation is complete.

During the distillation, add just enough 0·1*N* sodium hydroxide to the distillate to keep it alkaline to phenolphthalein.

Evaporate the alkaline distillate to small volume, but not to dryness, in a silver or platinum dish,

transfer to a 25- or 50-ml volumetric flask, and make up to volume. Make a preliminary determination on a 2- or 5-ml aliquot. Depending on the fluorine found, make a final titration, using either the balance of the solution (after re-evaporation to small volume), or a suitable aliquot chosen so that the titration will be 1–2 ml of standard thorium nitrate.

The titration is accomplished as follows: To the aliquot of the sample solution in a 50-ml beaker add 0·2*N* hydrochloric acid dropwise until the phenolphthalein is decolorised. Then add 3 drops of alizarin indicator, and continue the dropwise addition of dilute acid to a pure yellow colour. Do not add more than one drop of 0·2*N* acid in excess. Add 0·3 ml of monochloracetate buffer, and enough water to give a total of just 15 ml *at the end of the titration.* Add 15 ml of ethanol, and titrate from a 2- or 5-ml microburette with standard thorium nitrate.

Standardise the thorium nitrate against measured volumes of the standard sodium fluoride solution which have been distilled in exactly the same manner as sample solutions, *i.e.*, from 30 ml of 24*N* sulphuric acid containing 1 ml of perchloric acid, with the addition of potters' flint. With silicate rocks, which normally contain less than 0·5% of fluorine, a direct standardisation without distillation is adequate, once the satisfactory performance of the still has been established, for recovery of small amounts of fluorine is very close to 100%. Thus, in a typical standardisation 0·50, 1·00, and 2·00 ml of standard fluoride solution required 0·48, 0·98, and 1·90 ml of thorium nitrate after distillation, and 0·48, 0·95, and 1·95 ml directly.

It is quite necessary to have reference solutions to compare with the sample solution during titration, in order to detect the exact end-point. These are prepared by adding 0·00, 0·50, and 1·00 ml of 0·0001*M* thorium nitrate, freshly prepared by dilution of the 0·005*M* solution, to 50-ml beakers containing 14 ml of water, 15 ml of alcohol, 3 drops of indicator, and 0·3 ml of buffer. When high percentages of fluorine are determined, the unknown should be compared at the end-point with a titrated solution resulting from the distillation of a known weight of fluorine close to that contained in the sample, and an empirical standardisation of the thorium nitrate should be made. A sample of lepidolite which showed 7·88% F by this procedure, gave 7·56% when titrated and calculated in the usual way, using the thorium nitrate molarity obtained by direct titration of standard sodium fluoride.

Rapid determination of fluorine in silicate rocks

Fuse 0·200 g of rock powder with 2 g of sodium peroxide in an iron crucible. Leach the melt with 10–15 ml of water, and add 25 ml of phosphoric acid and 0·2 ml of perchloric acid. Transfer to the special still, stopper the steam inlet with a tube carrying a very slow current of air (1 bubble per sec) to prevent bumping, and heat to 135°. At this temperature start the steam flow, and allow the operating temperature to increase to 160–165° as registered on the thermometer. Collect about 125 ml adding 1% sodium hydroxide as necessary to keep the distillate alkaline to phenolphthalein. Determine fluorine as described above. With materials containing more than a few tenths of a per cent, a second 100 ml of distillate should be collected and treated separately.

A blank determination should be made, and the results corrected accordingly. A normal blank corresponds to about 0·02–0·03% F on a 0·2-g sample.

DISCUSSION

Experiment has shown that there is a rather narrow temperature range in which fluorine may be distilled completely and rapidly from sulphuric acid solution without appreciable volatilisation of the latter. This confirms the findings of Reynolds and Hill.[13] With the special still, the actual temperature of the sample solution is difficult to measure, because of the close proximity of the thermometer well to the trap drain and steam inlet, and heat losses within the well itself. An optimum temperature reading must be established for each still: only in this way can one be certain that harmful amounts of sulphate will not be contained in the distillates from actual samples. There is probably no satisfactory way of determining sulphate contamination in such distillates quantitatively, because of fluoride interference. Fluorine interferes, for example, in the chloranilic acid method of Bertolacini and Barney.[2]

The optimum operating temperature for each still is determined by passing steam through diluted sulphuric acid in the apparatus, exactly as in an actual determination except that no perchloric acid is added, collecting 10-ml fractions of distillate at gradually increasing temperature, and titrating them with 0·01*N* alkali. A typical set of results from this procedure is shown in Fig. 3. It is apparent that in this particular case,

the safe maximum operating temperature is reached at a thermometer reading of about 140°. Above 145°, the amount of acid in the distillate increases rapidly. For three different stills, the best operating temperatures were determined to be 138°, 143°, and 140°. The actual temperature of the sample solution is estimated to be about 5–10° higher than that registered on the thermometer.

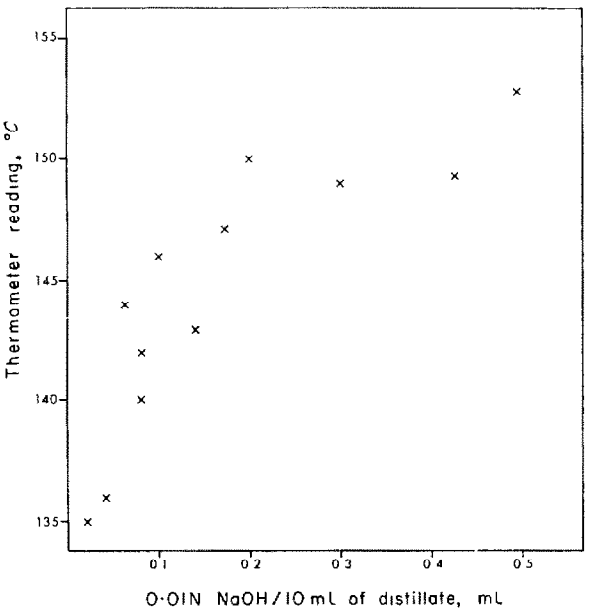


FIG. 3.—Determination of maximum operating temperature.
10-ml fractions of distillate from sulphuric acid were collected at gradually increasing temperature, and titrated with 0·01*N* alkali. Distillation rate, 3–4 ml per min.

Determining the lowest effective temperature is somewhat difficult. It appears to depend on incidental amounts of iron, aluminium, and other elements in the solution. With pure sodium fluoride distilled from 30 ml of 24*N* sulphuric acid containing 1 ml of perchloric acid, fluorine is quantitatively recovered in a relatively short time near the maximum permissible temperature, but incompletely in twice the time at temperatures only 5–10° lower (Fig. 4). The lower temperature does not result in appreciable lessening of the initial rate of recovery, but the last of the fluorine distils only slowly. This may arise from the presence of small amounts of complex fluorides which require the slightly higher temperature for their rapid dissociation, or it may be because fluoride absorption on the glass surfaces within the still is minimised by the passage of perchloric acid vapour with the steam. The former supposition is supported by the observation that filtrates derived from the treatment of rock samples vary widely in their behaviour when distilled at 130–135°, with incomplete recovery of fluorine as a rule, but at 140–145°, recovery is invariably rapid and complete. The more rapid recovery of fluorine when a little perchloric acid is present (as in the recommended procedure) supports the second supposition.

The temperature of the air bath during steam distillation is not critical, so long as condensation within the still is prevented. A thermometer suspended within the bath

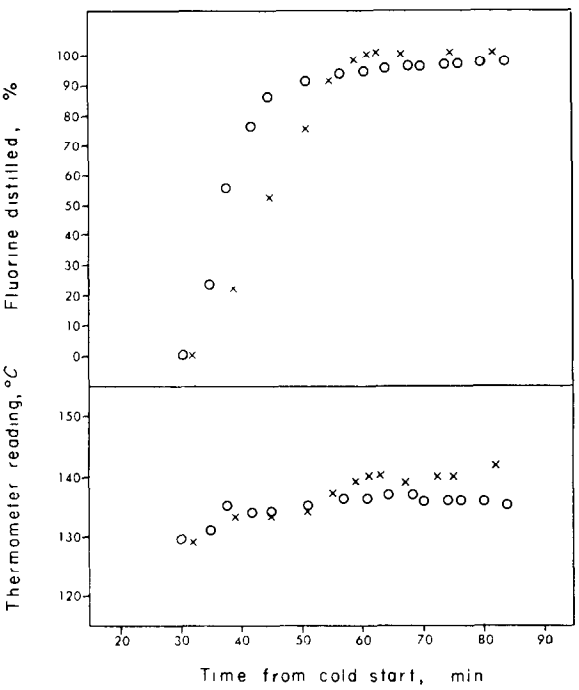


FIG. 4.—Effect of temperature on the steam distillation of fluorine.

Distillation of 3·39 mg of F from sulphuric acid containing a little perchloric acid: 10-ml fractions of distillate were collected and titrated with thorium nitrate as in the procedure, and the thermometer reading was recorded. A reading of 140° (corresponding to an estimated solution temperature of 150°) is required for rapid and complete recovery of fluorine.

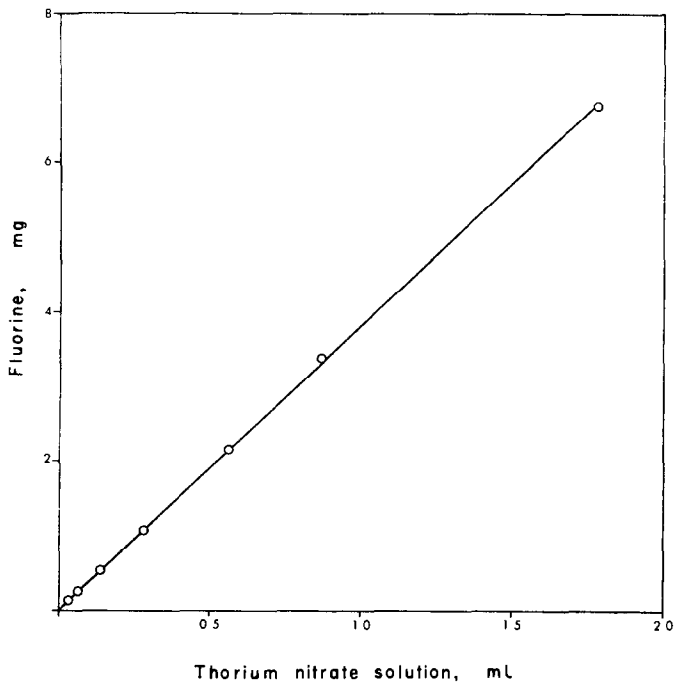


FIG. 5.—Titration curve in 50% ethanol solution.

The curve is essentially a straight line down to the limit of detection.

may register between about 85° and 105°, depending on the proximity of the bulb to the neck of the distilling flask.

Titration with thorium nitrate in 50% alcohol is much superior to the aqueous titration, especially when small amounts of fluorine are involved. The titration curve (Fig. 5) is very nearly a straight line through the origin. Less than 5 μg of fluorine can be detected with certainty. Precision is best when the titration is between 1 and 2 ml of thorium nitrate solution, that is with about 0·5 mg of fluorine. This amount can be determined with a precision of about 2% by the regular procedure, and 1% if special precautions are taken, as suggested in the procedure for samples containing high percentages of fluorine.

TABLE I.—COMPARATIVE RESULTS
(Martha Bailey, analyst)

Sample	Description	F, %	
		Found	Accepted value
1 E/S 1	quartz monzonite	0·129	0·12[a]
2 F/MC 17	migmatite	0·109	0·09[a]
3 E/P 1	tourmaline granite	0·249	0·24[a]
		0·251	
		0·256	
4 S/T 1	tonalite	0·077	0·07[a]
		0·079	
		0·076	
5 G/G 1	nepheline syenite	0·062	0·05[a]
6 I/C 2	hornfels	0·064	0·06[a]
7 S/A 1	eucrite	0·000	0·01[a]
		0·002	
8 E/M 1	diabase	0·053	0·05[a]
		0·057	
9 E/H 1	marine shale	0·089	0·07[a]
		0·086	
		0·091	
10 I/C 1	semi-pelitic schist	0·096	0·08[a]
G–1	granite	0·074	0·073[b]
		0·073	
		0·069	
W–1	diabase	0·031	0·02[b]
		0·030	
	syenite[c]	0·168	
		0·167	
		0·170	

[a] Consensus mean of results reported by R. P. Hollingworth in a paper presented at the Annual Meeting of the Canadian Institute of Chemistry, Montreal, Canada, August, 1961.

[b] Recommended value, U.S. Geological Survey Bulletin 1113.

[c] Standard sample, Canadian Association for Applied Spectroscopy; other results not yet available. This sample contains zirconium, which may lead to low recoveries of fluorine.

An advantage of the microtitration in 50% alcoholic solution, which is particularly evident when high percentages of fluorine are to be determined, is that only a small part of the distillate is used in the titration. This dilutes the small amount of sulphate present to the point where its effect is entirely negligible, and overcomes the difficulty, met with in some procedures, occasioned by the increasing interference of a given

amount of sulphate with increasing fluorine content of the solution. In the recommended method, sulphate interference is at its worst when the whole of the distillate is used for the titration. It is for this reason that separate 100-ml portions of distillate should be collected with unknown samples, and titrated separately.

TABLE II.—DETERMINATION OF FLUORINE AFTER DIRECT DISTILLATION FROM PHOSPHORIC ACID
(C. O. Ingamells and Martha Bailey, analysts)

Sample	F, %	
	Found	Accepted value
1 E/S 1	0·12	0·12
2 F/MC 17	0·07	0·09
3 E/P 1	0·23	0·24
	0·22	
4 S/T 1	0·07	0·07
5 G/G 1	0·05	0·05
6 I/C 2	0·07	0·06
7 S/A 1	0·01	0·01
8 E/M 1	0·05	0·05
9 E/H 1	0·07	0·07
10 I/C 1	0·07	0·08
syenite	0·19	0·17[a]
lepidolite	7·78[b]	7·88[a,b]

[a] Determined by the general method presented in this paper.

[b] 400 ml of distillate collected: standardisation of the thorium nitrate made by titrating a similar volume of distillate from standard fluoride solution.

The general procedure given above has been used for several years with a still of conventional design, sulphate entrainment having been controlled by distilling very slowly (less than 1 ml per min). The new still has greatly improved the performance of the method and reduced the time required for a determination. The rapid procedure involving distillation from phosphoric acid has not yet been extensively tested, but preliminary experiments and the results summarised in Table II indicate that it may be of great value in routine work with samples which are known to be free from interfering elements such as sulphur. Results are not as precise as with the general method given above, because blanks are not as reproducible, and the very small amount of phosphate in the distillate affects the titration adversely. As the fluorine content of the sample increases, these factors become less serious.

Some comparative results obtained by the general method are given in Table I. The first given result for each of the samples (except G-1 and W-1) was obtained before any knowledge as to the nature of the sample or its fluorine content was available to the analyst.

Acknowledgements—The author wishes to acknowledge the invaluable assistance of R. P. Hollingworth in the preparation of the manuscript, and of Martha Bailey, who carried out most of the determinations reported herein.

Zusammenfassung—Der Wirkungsgrad der Fluoriddestillation nach Willard und Winter kann verbessert werden, wenn statt Perchlorsäure Schwefel- oder Phosphorsäure verwendet wird. Phosphat und Sulfat müssen jedoch vom Destillate fern gehalten werden, da sie viele Methoden (einschliesslich der üblichen Thoriumtitration) zur Bestimmung des Flourides stören. Ein Apparat wird

beschrieben, der genaue Überwachung der Destillation gestattet und eine schnelle und vollständige Ansammlung des Fluorides in einem von Sulfat und Phosphat freien Destillat. Methoden werden mitgeteilt um Fluorid quantitativ aus Silikatgesteinen und Mineralen zu gewinnen und mit hoher Genauigkeit zu bestimmen.

Résumé—L'efficacité de l'entraînement à la vapeur du fluorure par la méthode de Willard et Winter peut être améliorée par l'utilisation de solutions d'acide sulfurique ou phosphorique au lieu de l'acide perchlorique. Cependant le sulfate et le phosphate ne doivent pas se trouver dans le distillat car ils gênent dans de nombreuses méthodes de dosage, y compris le titrage habituel au nitrate de thorium. On décrit un nouvel appareillage qui permet un contrôle efficace de la distillation et la récupération rapide et complète du fluor débarassé de quantités importantes de sulfate et de phosphate. On en tire des procèdés où les fluorures peuvent être extraits quantitativement des roches et minéraux siliciques et déterminés facilement avec exactitude et précision.

REFERENCES

[1] W. D. Armstrong, *J. Amer. Chem. Soc.*, 1933, **55**, 1741.
[2] R. J. Bertolacini and J. E. Barney II, *Analyt. Chem.*, 1958, **30**, 202.
[3] D. Dahle and H. J. Wichmann, *J. Assoc. Offic. Agric. Chemists*, 1936, **19**, 313, 320; 1937, **20**, 297.
[4] R. B. Ellestad, Unpublished method of the University of Minnesota Rock Analysis Laboratory, cited by I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*. The Macmillan Co., New York, 3rd. ed., 1952, p. 722.
[5] W. B. Estill and L. C. Mosier, *Analyt. Chem.*, 1955, **27**, 1669.
[6] F. S. Grimaldi, B. Ingram and F. Cuttitta, *ibid.*, 918.
[7] L. V. Haff, C. P. Butler and J. D. Bisso, *ibid.*, 1958, **30**, 984.
[8] J. I. Hoffman and G. E. F. Lundell, *J. Res. Nat. Bur. Stand.*, 1929, **3**, 581; Research Paper No. 110.
[9] R. P. Hollingworth, *Analyt. Chem.*, 1957, **29**, 1130.
[10] W. M. Hoskins and C. A. Ferris, *Ind. Eng. Chem., Analyt.*, 1936, **8**, 6.
[11] W. B. Huckaby, E. T. Welch and A. V. Metler, *Analyt. Chem.*, 1947, **19**, 154.
[12] S. Megregian and I. Solet, *J. Amer. Water Works Assoc.*, 1953, **45**, 1110.
[13] D. S. Reynolds and W. L. Hill, *Ind. Eng. Chem., Analyt.*, 1939, **11**, 21.
[14] E. D. Schall and H. G. Williamson, *J. Assoc. Offic. Agric. Chemists*, 1955, **38**, 454.
[15] H. R. Shell and R. L. Craig, *Analyt. Chem.*, 1954, **26**, 996; *U.S. Bur. Min. Report of Investigations*, 5158, January 1956.
[16] O. D. Smith and T. D. Parks, *Analyt. Chem.*, 1955, **27**, 998.
[17] E. Tiedemann, *Z. analyt. Chem.*, 1956, **150**, 1.
[18] T. K. Wadhwani, *J. Indian Inst. Sci.*, 1953, **34**, 135.
[19] R. Valach, *Talanta*, 1961, **8**, 629.
[20] *Idem, ibid.*, 443.
[21] H. H. Willard and O. B. Winter, *Ind. Eng. Chem., Analyt.*, 1933, **5**, 7.

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CONTINUOUS DETERMINATION OF URANIUM IN IMPURE SOLUTIONS BY GAMMA SPECTROMETRY

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Summary—The non-destructive determination of uranium, by measurement of the 184-KeV gamma ray activity arising from the decay of uranium-235, has been extended to the continuous monitoring of impure plant solutions. Interference in the gamma spectrometric measurement at 184 KeV by the radioactive decay products of uranium is eliminated by means of an error signal. Measurement of the decay product gamma activity at higher energies is used to produce a signal which is injected, suitably proportioned and phased, into the measurement channel. An instrument is described which is suitable for the monitoring of uranium streams containing 5–30% w/v of natural uranium. Gross changes in the acidity and in the impurity content of the uranium stream have no appreciable effect on the indicated uranium concentration.

INTRODUCTION

THE operation of a uranium purification process requires that the concentration of uranium at various points should be known at any time. The delays unavoidably caused in the application of conventional analytical techniques may, in some instances, be an embarrassment in process control and point to the advantages to be gained from 'in line' automatic methods of analysis. In the ultimate such automatic analysers should be sufficiently rapid in response and should have an output in a form suitable for the operation of a servo mechanism capable of correcting for undesired changes as they occur.

The measurement of the gamma ray activity of uranium-235 has been used for its quantitative determination by gamma spectrometry.[1–11] This technique had been shown previously to offer a sufficiently precise and rapid method of non-destructive measurement to warrant further study as the basis for a continuous monitor. A comparison of the relative merits of gamma spectrometry with the more established technique of gamma absorptiometry[12–16] showed that, for impure solutions, the interference caused by gamma attenuation in the impurities would be smaller at the higher energies used in the gamma spectrometric measurement.[17]

The gamma spectrum of natural uranium comprises three main components. A gamma photopeak is observed at 90 KeV, which arises in the decay of uranium-238, uranium-235 and daughter activities. Two further photopeaks are observed at 143 KeV and 184 KeV arising from the decay of uranium-235 and, in addition, there is a continuum of activity to greater than 2 MeV. This is caused by Bremsstrahlung radiation arising from the interaction of decay product beta particles with the uranium.[18] The proportion of gamma activities at 90 KeV and in the continuum vary according to the extent of equilibrium of the uranium daughter products. The 184-KeV and 143-KeV photopeaks are influenced by the daughter product activities only to the extent of the small portion of the continuum included in them. Fig. 1 shows the gamma spectra of uranium in full equilibrium with daughter activities and of freshly purified uranium containing no daughter product activity. From these spectra it can be seen that a true

measure of the uranium-235, and hence of the total uranium in the case of a fixed isotopic composition, as in natural uranium, can be obtained by measuring only the 184-KeV and 143-KeV photopeaks and correcting for the continuum.

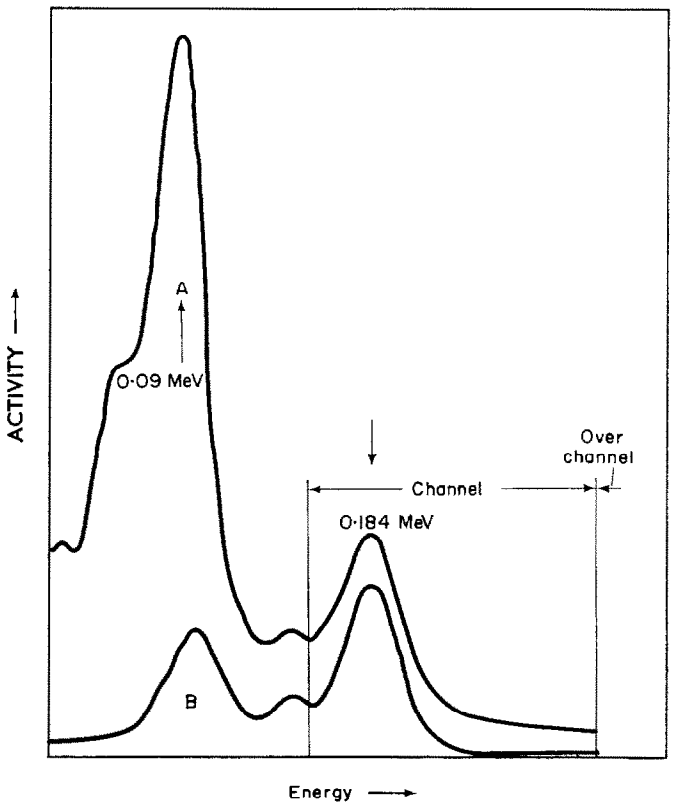


FIG. 1.—Gamma spectra of natural uranium:
A—equilibrium daughter activities,
B—no daughter activities.

The resolution of a good thallium activated sodium iodide crystal is adequate to differentiate between the 90 KeV and 184 KeV activities and it is, therefore, possible to measure the 184-KeV activity without interference from that at 90 KeV. This avoids the effects of the varying daughter product activity present in the 90-KeV photopeak.

The continuum of Bremsstrahlung radiation is present over the whole of the uranium spectrum and measurements in the energy region of the 184-KeV photopeak inevitably include a portion of the continuum. The continuum is, however, directly proportional to the decay product activity and measurement in any part of the spectrum away from the uranium photopeaks can be used to correct any other part, provided that the proportionality is known. A correction of this type had been used previously by making two measurements on a sample, one at 184 KeV to obtain the required uranium activity and another at 300 KeV to obtain the correction for daughter activity at 184 KeV. To do this continuously a two-channel gamma

spectrometer measuring simultaneously at the two energy levels is required. The single channel instrument A.E.R.E. type 1168 does, however, have an auxiliary output giving an integrated measure of all activities greater than the channel being measured. If this could be used for measurement of the continuum considerable complication could be avoided.

A plot of uranium concentration versus gamma activity at 184 KeV gives a curve. The cause of the curvature is self absorption of the gamma rays in the uranium.

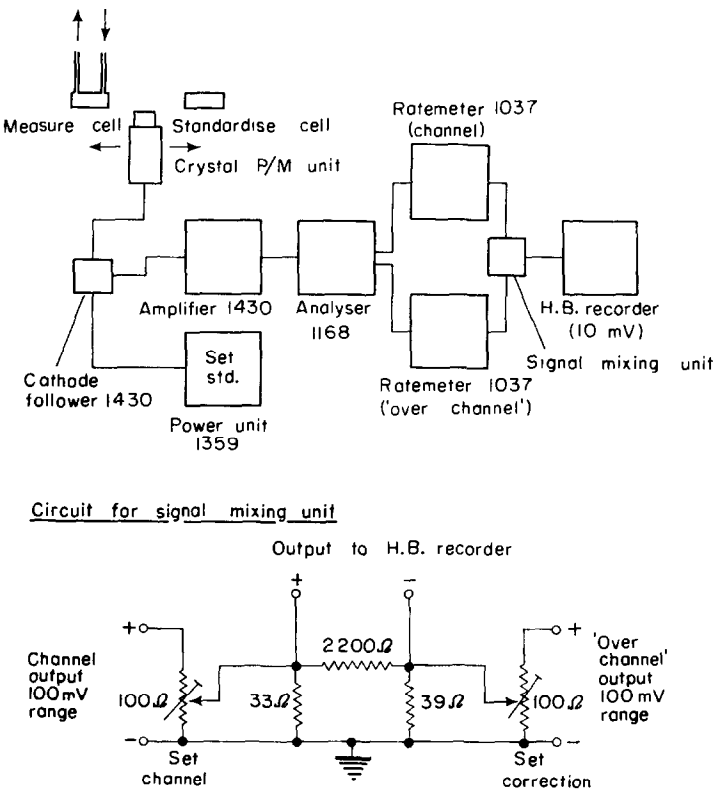


FIG. 2.—Layout of equipment and associated circuits.

Being predominantly caused by the photoelectric process, the absorption is proportional to atomic number to the fifth power (Z^5)[19] and hence falls off very rapidly for elements of lower atomic number. The effects of impurities on these gamma ray measurements would, therefore, be expected to be very small.

These considerations led to the conclusion that a single-channel gamma spectrometer could form the basis of a relatively simple and sufficiently precise automatic analyser for uranium. The curvature in the response to uranium must be kept within reasonable limits and other gamma activities must not be present in the parts of the spectrum used in the measurement of the 184-KeV photopeak and the continuum.

EXPERIMENTAL

Electronic equipment

The proposed layout of the electronic equipment shown in Fig. 2 was based entirely on standard A.E.R.E. type units. For the experimental work in assessing the technique, the two ratemeters were

replaced by scaling units to enable more precise measurements to be made. The photomultiplier anode load was made 100 KΩ and the amplifier integrating and differentiating time constants were both set at 0·32 μsec. This combination had previously been shown to give the optimum pulse size consistent with short paralysis time (<10 μsec overall) for counting uranium gamma activity.

Selection of counting conditions

With the amplifier attenuation at zero, the high tension supply to the photomultiplier was increased until the uranium spectrum from a sample of natural uranium appeared at the pulse analyser, with the 184-KeV photopeak in the centre of the analyser base line.

For the instrument to fulfill the requirements for uranium determination, a number of conditions had to be satisfied:

(1) The channel used in measuring the 184-KeV peak must not contain any contribution from the 90-KeV peak.

(2) The integrated output measuring the continuum must not contain any contribution from the 184-KeV peak.

(3) The channel used in measuring the 184-KeV peak must be as wide as possible to obtain the highest possible counting rate and hence the best precision of measurement.

(4) The integrated output measuring the continuum for correction purposes must have a sufficiently high output to avoid seriously affecting the precision of the corrected channel output.

Condition (4) must be met by a suitable choice of detector crystal when using the integrated output of a single channel analyser unit, as there is no means of varying the channel width used for measurement of the continuum. In practice the 1″ thick by 1·5″ diameter crystal used was found to give an adequate output at the higher gamma energies. The other conditions were arrived at by studying the gamma spectra for uranium in equilibrium with, and after the separation of, daughter activities. Condition (1) was readily arrived at by setting the lower bias at 150 KeV in the valley between the 143-KeV and 184-KeV photopeaks. Conditions (2) and (3) then required only that the channel width was set such that the upper bias represented an energy well clear of the 184-KeV peak, a point at 300 KeV was selected for this as shown in Fig. 1.

A gamma spectrometer is inherently an unstable device, small changes in photomultiplier gain, overall amplification, photomultiplier high tension supply, *etc.*, giving rise to a lateral displacement of the observed spectrum up or down the energy scale. These effects are minimised by careful stabilisation of the electronic circuits but nevertheless they still exist. It is, therefore, necessary to choose conditions which will minimise the effects of electronic or other changes on the measurements if good stability of operation is to be attained. The measuring conditions chosen are seen to represent the best compromise in this respect. Drift of the upper bias point adds or subtracts only a minor contribution to the channel or over channel outputs. Drift of the lower bias point has a negligible effect on the over channel output but a more serious effect on the channel output, because of the relatively high activity in this part of the spectrum. The effect of drift on the channel output is, however, a minimum for the point selected in the valley between the 143-KeV and 184-KeV peaks.

Measuring cell

Lengths of stainless steel and glass tubing of various sizes were filled with uranium solutions of different concentrations and the gamma activities measured. The results showed that for uranium concentrations greater than 10% w/v self-absorption effects were prohibitive; below 10% w/v, the counting rates were too low to be of value.

Replacement of the tubing with a flat cell of the same diameter as the crystal (1·5″) showed a very considerable increase in counting rates and indicated that the self-absorption effects, and hence non-linearity, could be kept sufficiently small provided that the thickness of the cell was limited.

A series of experiments was undertaken to verify this, using uranium solutions of different concentrations, both in equilibrium and after removal of daughter products. Measurements were made on various thicknesses of each solution. The results of these measurements are shown in Fig. 3, and led to the following conclusions:

(1) Selection of a suitable cell thickness would enable a range of 5–30% w/v uranium to be covered (using a 1″ × 1·5″ crystal) with a non-linearity of less than 10%.

(2) Non-linearity was slightly worse in the measurement of uranium containing no decay product activities.

(3) Differences between the net counting rates for equilibrium and freshly extracted uranium were proportional to the counting rate of the 'over channel' integrated output for the uranium in equilibrium. This showed that the counting rate obtained for the continuum could be used in correcting for daughter activity interference.

Measuring cell assembly for 'in line' monitoring

For the 'in line' monitoring of uranium a flow-through measuring cell is required having a 'window' essentially transparent to the gamma rays. A cell was constructed in welded polythene and tested to 50 psi water pressure. This cell was designed from the data obtained previously for a range of 5–30% w/v uranium, the dimensions being shown in Fig. 4.

The cell was inserted in one side of the lead shielded assembly shown in Fig. 4 with a polythene cell of similar but arbitrary size in the opposite side. The crystal-photomultiplier was mounted on a swinging arm with locating stops such that the crystal could be brought accurately beneath either cell.

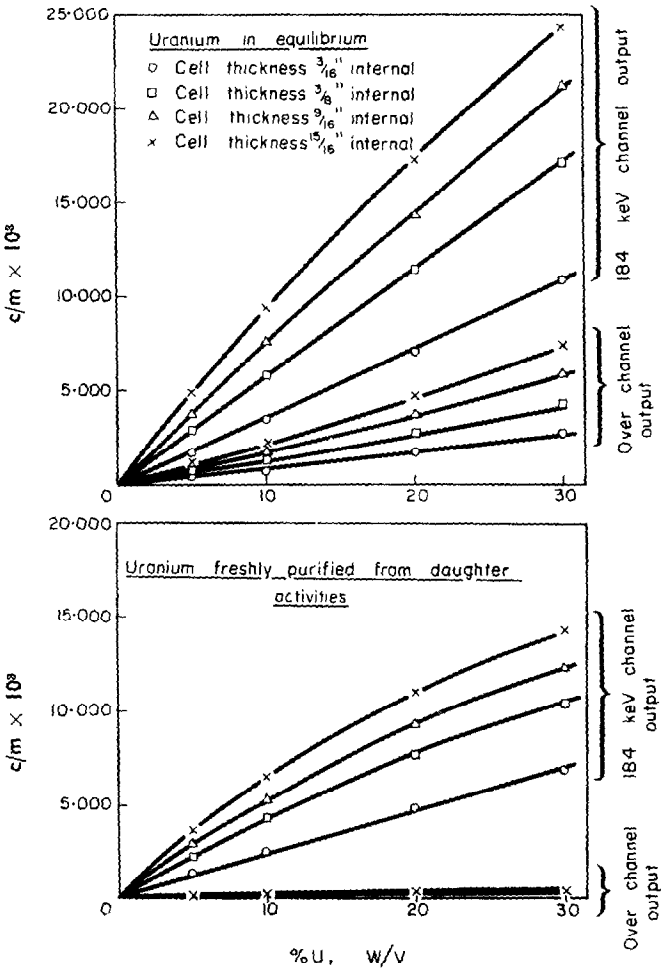


FIG. 3.—Effect of cell thickness on calibration.
(The lowest thick curve represents four separate curves.)

Uranium solution was then added to the second cell until the counting rate was the same as that obtained from the measuring cell when filled with a 20% w/v uranium solution. The second cell was then sealed and became a permanent standard, equivalent to 20% w/v uranium in the measuring cell. This procedure was adopted to avoid the difficulties in making two exactly matching cells for measurement and standardisation.

Daughter product activity correction ratio

Solutions of uranium at a concentration of 20% w/v, one in equilibrium with daughter products and the other freshly-extracted, were admitted to the measuring cell and their activities measured.

The following data was obtained:

Background with cell empty, channel output = 164 cpm
Background with cell empty, 'over channel' output = 282 cpm
20% w/v uranium in equilibrium, channel output = 6488 cpm
20% w/v uranium in equilibrium, 'over channel' output = 1695 cpm
20% w/v uranium freshly extracted, channel output = 4486 cpm
20% w/v uranium freshly extracted, 'over channel' ouptut = 325 cpm .

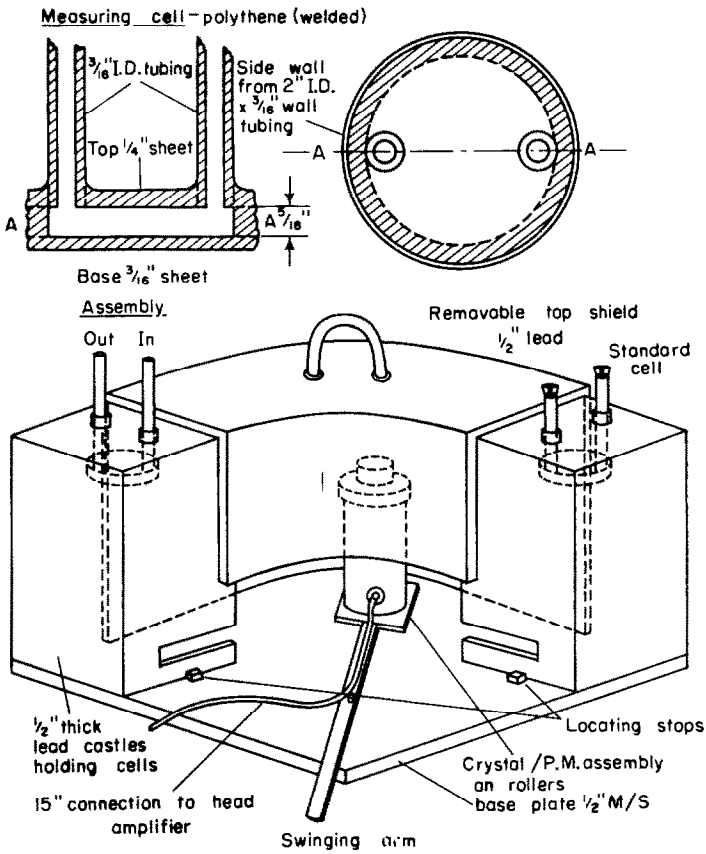


FIG. 4.—Measuring cell and cell assembly.

If the true reading for the uranium activity is y cpm and the ratio by which the "over channel" output must be increased to give the required correction is x, then for equilibrium uranium

$$6488 - 1695x = y \tag{1}$$

and for extracted uranium

$$4486 - 325x = y \tag{2}$$

Subtracting

$$1370x = 2002$$

and $x = 1{\cdot}46$ (background effects cancel).
Substituting in (1):

$$y = 6488 - 2478 = 4010.$$

For the output of the monitor to read 20%, the output from the channel must give a reading of

$$\frac{20 \times 6488}{4010} = 32{\cdot}4\% \text{ for an equilibrium 20\% uranium solution.}$$

This reading then requires reduction to 20·0% by the signal from the 'over channel' output.

Correction circuit

The scaling units were replaced by the two ratemeters, one measuring the channel output and the other the 'over channel' output. The output from the ratemeters were connected in opposition using the circuit shown in Fig. 2. This enabled a varied output to be obtained from each with the strip chart recorder measuring the difference between the two. The instrument was then set to measure the 20% w/v equilibrium standard in the standardise cell and, with the 'over channel' output control at zero, the channel output was increased to give a reading of 32·4 on the recorder. The 'over channel' output was then increased until the recorder reading was reduced to 20·0. The two ratemeter output controls were then locked in these positions.

Statistical variations

The statistical variation in a ratemeter output is given by:

$$\sigma = \pm \frac{100}{\sqrt{2nT}} \tag{20}$$

where n is the mean pulse rate/sec and T is the integrating time in sec.
A 20% uranium solution in equilibrium gives

channel output = 108 cps
'over channel' output = 28 cps,

and at 30%

channel output = 162 cps
'over channel' output = 42 cps.

The longest time constant available on the ratemeter used (A.E.R.E. type 1037C) on the X 1000 range is 40 sec. This gives rise to rather wide statistical variations at these counting rates and was therefore increased, by increasing the integrating resistance of the ratemeter, to 160 sec.

For the combined output where the over channel output is increased by 1·46 before applying it as the correction:

$$\text{At } 20\%,\ \sigma = \pm\sqrt{\left(\frac{100}{\sqrt{2 \times 108 \times 160}}\right)^2 + 1{\cdot}46 \times \left(\frac{100}{\sqrt{2 \times 28 \times 160}}\right)^2}\ \%$$

$$= \pm \sqrt{0{\cdot}28 + 1{\cdot}64}\%$$

$$= \pm 1{\cdot}38\%$$

$$\therefore 3\sigma = \pm 4{\cdot}14\% \equiv \pm 0{\cdot}8\% \text{ uranium.}$$

$$\text{At } 30\%,\ \sigma = \pm\sqrt{\left(\frac{100}{\sqrt{2 \times 162 \times 160}}\right)^2 + 1{\cdot}46\left(\frac{100}{\sqrt{2 \times 42 \times 160}}\right)^2}\ \%$$

$$= \pm \sqrt{0{\cdot}193 + 1{\cdot}09}\%$$

$$= 1{\cdot}13\%$$

$$\therefore 3\sigma = \pm 3{\cdot}39\% \equiv \pm 1{\cdot}0\% \text{ uranium.}$$

For solutions containing no decay product activity, the second term of the expression becomes negligible when the precisions (3σ) become 0·3 and 0·4% uranium at 20% and 30% uranium, respectively.

Further improvement in the precision of measurement could be obtained in two ways, either by further increasing the time constant, or by the use of a larger diameter crystal and measuring cell giving an increased counting rate. Further increase in the time constant would make the instrument response too sluggish, for the 160 sec used a 99% response is attained in about 4 C.R. or approximately 10 min and it was not felt desirable to increase this any further. Larger crystals were not available at the time.

Laboratory trials of the complete monitor

The following trials were carried out in the laboratory:
(1) Long term stability.
(2) Uranium calibration.
(3) Effect of varying the amount of daughter product activity present in the uranium.
(4) Effect of impurities.

The results of these trials are shown in Table I and Fig. 7(a) and (b).

TABLE I.—Laboratory trials of the complete monitor.

Solution measured	Object	Reading obtained U w/v	Observation
10% w/v U Equilibrium UXI	Calibration	10·2%	Within expected error
20% w/v U Equilibrium UXI	Calibration	19·8%	Within expected error
30% w/v U Equilibrium UXI	Calibration	30·0%	Within expected error
40% w/v U Equilibrium UXI	Calibration	37·3%	Low, due to self absorption
20% w/v U Equilibrium UXI	Stability check	20·0 ± 0·5%	20-hr run within expected error
30% w/v U Equilibrium UXI	Stability check	29·5 ± 0·75%	16-hr run within expected error
30% w/v U Equilibrium UXI	Stability check	29·8 ± 0·75%	20-hr run within expected error
20% w/v U No UXI	Stability and effect of UXI	20·0 ± 0·3%	16-hr run within expected error. Daughter product correction satisfactory.
25% w/v U Equilibrium UXI No free acid	Effect of acidity	24·8%	
25% w/v U Equilibrium UXI in 10*N* HNO_3	Effect of acidity	24·5%	No effect from HNO_3
25% w/v U containing 50% Fe on U basis	Effect of impurities	25·75	Slight positive error

The measuring cell thickness of 5/16″ had been chosen to work over a range of up to 30% w/v. uranium and, therefore, the self absorption effect observed at 40% w/v was expected. The reading obtained in the presence of iron is considered to be satisfactory in view of the high impurity content simulated. The reason for the error, in the presence of impurities, being in the positive direction is not fully understood but is believed to arise from the same effect which produces the difference in linearity between equilibrium and freshly extracted uranium apparent from Fig. 3.

PLANT-SCALE TRIAL OF THE MONITOR

The monitor was assembled on the plant with the measuring cell in parallel with the line feeding from a crude uranyl nitrate stock tank to the solvent purification system. Flow through the cell was controlled by a stopcock and was set at approximately 2 litres/min. A general view of the installation is shown in Fig. 5.

Several 24-hr runs were made in the standardise position, *i.e.* continuously measuring the 20% w/v uranium (equivalent) solution in the standardising cell. These showed that the stability on the plant, where temperature fluctuations and mains voltage variations were more likely to occur than in the laboratory, was as good as had been obtained in the laboratory. This indicated that the monitor would not require standardising more frequently than once each day.

The line was then monitored for a period of 10 days, the instrument being standardised each day. Standardisation entailed moving the crystal assembly to the standardise position, allowing the reading to settle, and then adjusting the high tension supply to the photomultiplier if the reading was outside the range 20 ± 0.5%. Adjustment was only required on three occasions during the 10 days and on these the reading was within 20 ± 1.0%.

Samples were taken from the line every 8 hr during the 10 days and analysed

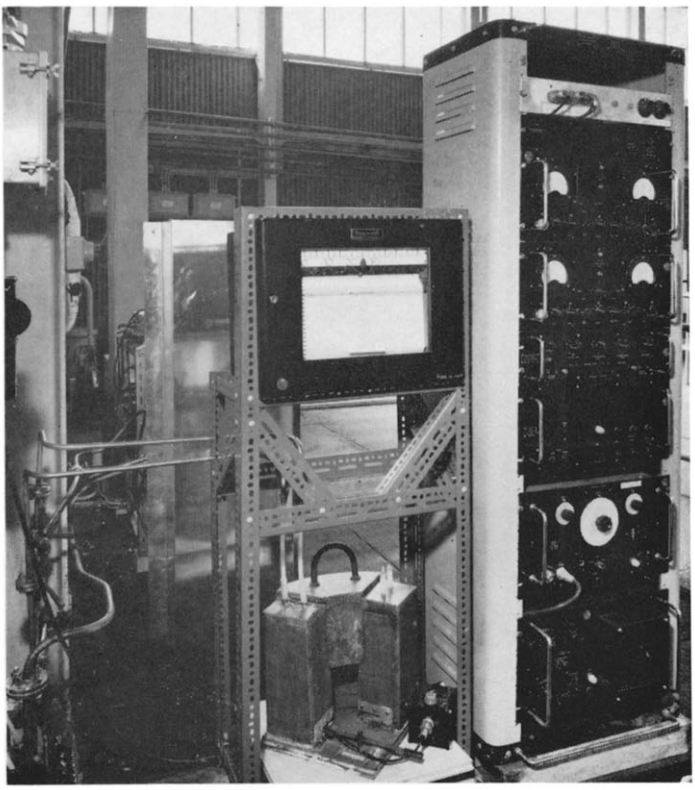
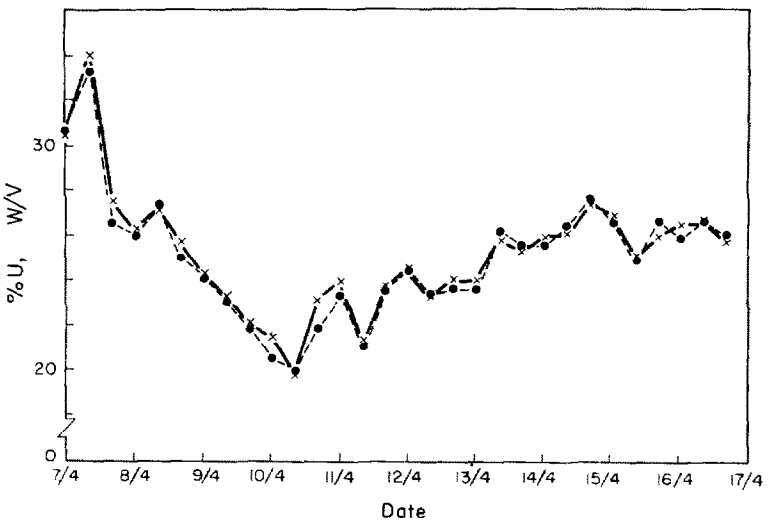


FIG. 5.—General view of installation.

chemically for uranium content by a gravimetric procedure. The comparison between the results read from the monitor strip chart and the chemical analyses are shown in Fig. 6. A record of the output from the recorder during 24 hr continuous operation is reproduced in Fig. 7(c).



Date	Time	%U, W/V	
		γ Spec.	Chem.
7/4	0730	30·7	30·5
7/4	1530	33·3	34·0
7/4	2330	26·5	27·3
8/4	0730	26·0	26·1
8/4	1530	27·3	27·3
8/4	2330	25·0	25·7
9/4	0730	24·0	24·2
9/4	1530	23·0	23·2
9/4	2330	21·8	22·0
10/4	0730	20·5	21·5
10/4	1530	20·0	19·8
10/4	2330	21·8	23·1
11/4	0730	23·3	23·9
11/4	1530	21·0	21·2
11/4	2330	23·5	23·6

Date	Time	%U, W/V	
		γ Spec	Chem.
12/4	0730	24·3	24·3
12/4	1530	23·3	23·2
12/4	2330	23·5	23·9
13/4	0730	23·5	23·8
13/4	1530	26·0	25·7
13/4	2330	25·5	25·3
14/4	0730	25·5	25·8
14/4	1530	26·3	26·1
14/4	2330	27·5	27·3
15/4	0730	26·5	26·8
15/4	1530	24·8	24·8
15/4	2330	26·5	25·9
16/4	0730	25·8	26·4
16/4	1530	26·5	26·4
16/4	2330	26·0	25·6

FIG. 6.—Uranium content—crude uranyl nitrate stock tank:
—X—X—chemical analysis.
– –O– –O– –gamma spectrometer.

APPLICATIONS

The gamma spectrometer has been applied here to the monitoring of impure solutions, arising from the dissolution of uranium concentrate in nitric acid, over a concentration range of 5–30% of natural uranium. Suitable measuring cell design and measuring crystal size would extend this range, but for natural uranium, the instrument is essentially a high concentration measuring device. It is doubtful whether a concentration of natural uranium much below 1% w/v could be usefully measured.

In measuring enriched uranium concentration, the sensitivity increases in proportion to the enrichment and the range of the instrument could be extended

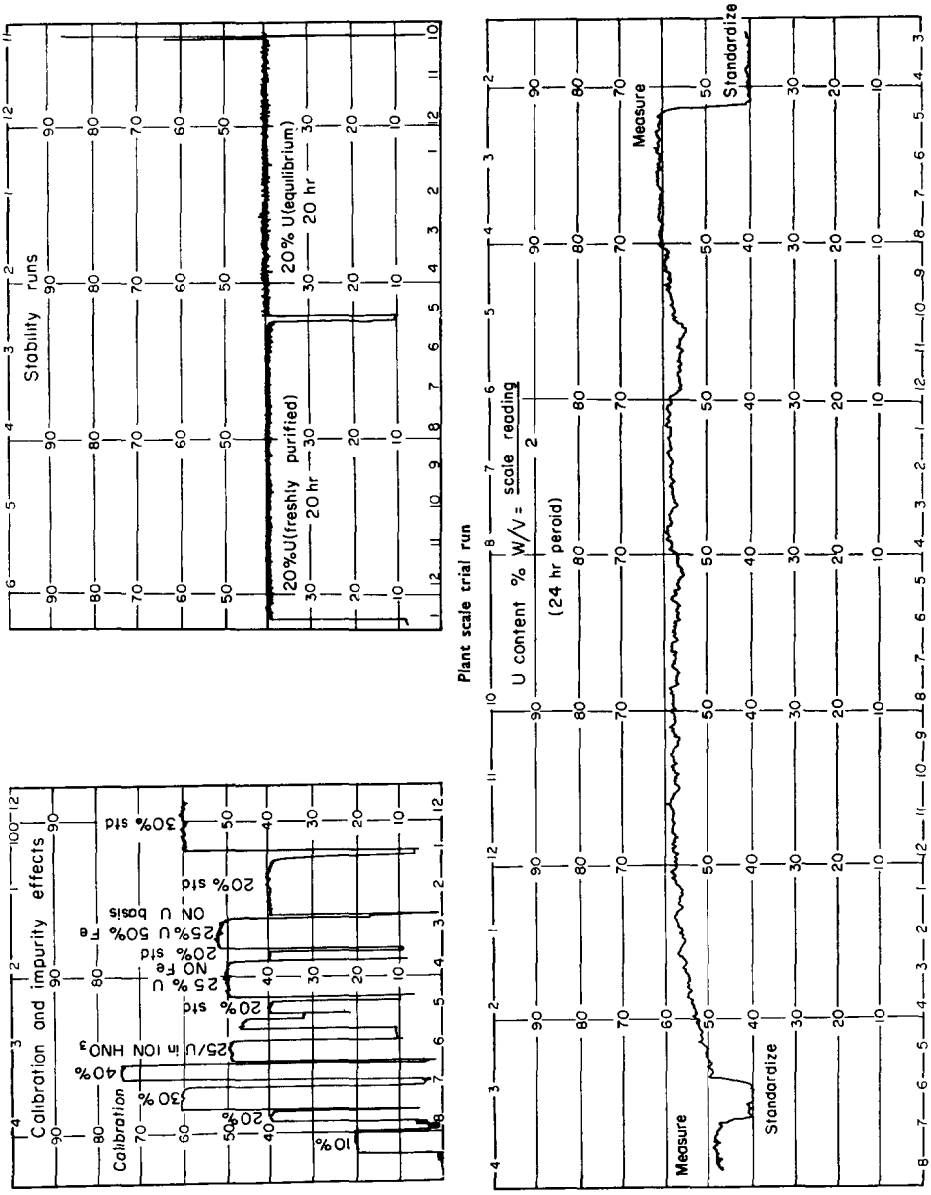


FIG. 7.—(a) Calibration and impurity effects. (b) Stability runs. (c) Plant-scale trial run.

considerably, down to the ppm. ranges. A number of enriched uranium residues are, however, known to contain other radioactive isotopes arising from thorium-228 and daughters as well as, in some cases, disproportionately high uranium daughter activity concentrations. A careful study of the effect of these would, therefore, be required.

No consideration has been given here to the effect of fission products on the principle of correction used in the monitor. There is no reason why the uranium daughter activity correction should not include a correction for the Compton scattering from fission product activity provided it is not too high. Gamma activity from fission products with an energy in the region of 184 KeV would, however, not be corrected for and could be the cause of considerable error in uranium measurements.

There is no evidence in the decay schemes for plutonium isotopes that these would cause direct interference. Previous work had shown that thorium in concentrations up to 2% on a uranium basis has no significant effect on gamma ray measurements as used in the monitor.

The continuous measurement of uranium should be possible in a number of different fields in uranium processing using the modified gamma spectrometer described. In particular, freedom from the effects of impurities, changes in acidity or uranium solvent, together with the stability of the instrument and its comparative simplicity make it compare favourably with other methods of continuous uranium measurement. A direct electrical signal representing uranium concentration is obtained for servo control should this be contemplated. The full response time of the monitor described is approximately 10 min. Whether this is sufficiently rapid for automatic plant control would require special consideration in the application to a particular plant.

The monitor was installed to give a continuous record of the uranium concentration on one plant line. There is no reason why one monitor should not be used to give an intermittent record on a number of plant lines. The liquor from each line could be fed to a simple valve system connected to the measuring cell and each line switched in as desired. The economic advantages of a system of this type are obvious, although some consideration would have to be given to the transit time if the feed lines to the monitor were unduly long.

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Zusammenfassung—Die nichtdestruktive Bestimmung von Uran (durch Messung der 184 KeV Aktivität des Zerfalls von 235 Isotopen) wurde ausgedehnt um die kontinuierliche Regelung von Lösungen im Fabriksbetriebe zu erzielen. Störung der gammaspektrometrischen Messung bei 184 KeV durch radioaktive Zerfallsprodukte des Urans wird mittels eines Fehlersihnals ausgeschaltet. Messung der Gammaaktivität der Zerfallsprodukte bei höherer Energie wird benutzt um ein Signal von geeigneter Grösse und Phase im Messkanal zu induzieren. Ein Instrument zu automatischen Strömungsregelung von Uranlösungen mit 5-30% (Gewicht/Volum) an natürlichem Uran wird beschrieben. Änderungen im Gehalt an Säure und Verunreinigungen haben keinen merkbaren Einfluss auf die Anzeige der Urankonzentration.

Résumé—Le dosage non destructif de l'uranium, par mesure de l'activité du rayonnement gamma de 184 KeV provenant de la dégradation de l'isotope 235, a été étendu au contrôle continu de solution de plante impure. Dans la mesure spectrométrique gamma à 184 KeV, l'interférence des produits de dégradation radioactifs de l'uranium est éliminée au moyen d'un signal d'erreur. La mesure de l'activité gamma du produit de dégradation aux très hautes énergies est utilisée pour produire un

signal qui est injecté dans le canal de mesure, en proportion convenable et en phase. Les auteurs décrivent un instrument qui convient au contrôle de courants d'uranium contenant de 5 à 30% (poids/volume) d'uranium naturel. De grandes variations d'acidité et de teneur en impureté du courant d'uranium n'ont pas d'effet appréciable sur la concentration d'uranium indiquée.

REFERENCES

[1] W. B. Wright, *et al.*, Gamma count estimation of enhanced uranium concentration in solution Y-1087, 1954.
[2] D. G. Miller, A non destructive method for the determination of 235 uranium in uranium metal slugs. HW-39969, 1955.
[3] G. H. Morrison and J. F. Cosgrove, *Analyt. Chem.*, 1957, **29**, 1770.
[4] M. E. Jacobs, Monitoring of material of low 235 uranium assay through gamma radiation energy separation. G.A.T.-254, 1958.
[5] S. D. Nelson, A gamma spectrometric determination of 235 uranium. MCW-1410, 1958.
[6] S. A. Reynolds and J. S. Eldridge, Uranium 235 abundance by gamma spectrometry. CF-57-1-3.
[7] D. G. Miller and M. B. Leboeuf, Determination of 235 uranium in 235 uranium- 238 uranium mixtures. HW-28634.
[8] J. W. Wachter and W. B. Wright, Measurement of uranium concentrations in U-Al alloy by gamma counting. Y-1080.
[9] E. L. Upson and D. G. Miller, A gamma counting method for the determination of 235 uranium in enriched uranium. HW-47867.
[10] C. A. Meinz and B. D. La Mont, The determination of 235 uranium in low enriched, non irradiated UO_2 pellets by gamma ray spectrometry. Conference on Analytical Chemistry in Nuclear Reactor Technology, Gatlinberg, U.S.A., Oct., 1960.
[11] R. C. Reinke, Routine analysis of enriched uranium with a gamma pulse height analyser. TID-7581.
[12] W. L. Maddox and M. T. Kelley, *Talanta*, 1959, **3**, 172.
[13] M. B. Leboeuf, D. G. Miller and R. E. Connally, *Nucleonics*, 1954, **12**, 18.
[14] D. H. Thurnau, *Analyt. Chem.*, 1957, **29**, 1772.
[15] F. D. Seymour, Density determination of uranium pulp and uranyl solutions by gamma ray absorptiometry. A.E.R.E. EL/R. 2269.
[16] Connally, Upsen, Brau and Brauer. Uranium analysis by gamma absorptiometry. HW-54438.
[17] U. Fano, *Nucleonics*, 1953, **11**, 8.
[18] D. K. Cartwright and E. J. Robbins, *J. Inorg. Nuclear Chem.*, 1960, **12**, 373,.
[19] O. R. Frisch, *The Nuclear Handbook*. George Newnes Ltd., London, 1958.
[20] G. Friedlander and J. W. Kennedy, *Introduction to Radiochemistry*. Chapman and Hall Ltd., London, 1949.

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PRELIMINARY COMMUNICATIONS

The use of oxycellulose for the collection of traces of metals: Qualitative investigations

(*Received* 14 *November* 1961. *Accepted* 28 *February* 1962)

IN previous work[1] the metal-binding capacity of cotton wool was investigated. The cotton wool was suitable for the collection of heavy metal ions which were contaminants of different solutions. Some experiments showed that oxycellulose was better for this purpose, therefore in our later work oxycellulose was used for the collection of such metals as Ag^{+}, Al^{3+}, Ba^{2+}, Bi^{3+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} from very dilute solutions.

TABLE I—QUALITATIVE INVESTIGATION OF OVERNIGHT COLLECTION OF METAL IONS ON OXYCELLULOSE FIBRILS.

Ion	Amount of ion collected (μg) from 1000 ml of distilled water or 10^{-4}% salt solutions* using 3 mg of oxycellulose	Spot tests used
Ag^{+}	10	*p*-Dimethylamino-benzylidenerhodanine[3]
Al^{3+}	1	Alizarin S[3]
Ba^{2+}	10	Sodium rhodizonate[3]
Bi^{3+}	5	Cinchonine and potassium iodide[3,4]
Cd^{2+}	10	Hydrogen sulphide
Co^{2+}	1	Ammonium thiocyanate in acetone[4]
Cu^{2+}	1	Rubeanic acid[3]
Fe^{2+}	1	α:α'-Bipyridyl[3]
Fe^{3+}	1	Potassium ferrocyanide[3,4]
Mn^{2+}	1	3:3'-Dimethylnaphthidine[3,4]
Ni^{2+}	1	Dimethylglyoxime[3,4]
	5†	
Pb^{2+}	1	Sodium rhodizonate[4]
Zn^{2+}	1	Mercury thiocyanate[4]

* NaCl, $NaNO_3$, NH_4Cl, NH_4NO_3
† from 5000 ml distilled water

Oxidised cellulose was prepared by alkaline hypobromite treatment of cotton wool, as described previously.[1] The pure oxidised cellulose, called oxycellulose, could be dispersed in distilled water to fibrils of 0·5–1 mm by shaking. These fibrils, suspended in 100, 1000, 5000 and in some cases in 10,000 ml of distilled water or very dilute inorganic salt solutions (10^{-4}%) at pH 5–6, gathered the metal ion contaminants of the solution on their surface. Even 1 μg of the above mentioned metal ions from 1000 ml distilled water, *i.e.* when the limit of the dilution was $1:10^{9}$, could be collected on 3 mg of oxycellulose. For qualitative purposes it was sufficient to shake the solutions, containing oxycellulose fibrils, on a shaking machine for 1 hr or put them aside overnight (see Table I). The reaction occurring between the metal ions and the carboxyl groups on the surface of the oxycellulose at pH 5–6 is called ion exchange according to the literature.[2] For the present we prefer to leave open the question as to whether the mechanism of the metal-binding is ion exchange or adsorption.

A simple and fast method was worked out for the filtration of the suspended oxycellulose fibrils. A sintered-glass filter stick, 5 mm in diameter, was dipped into the solution and the fibrils were collected on the filter by means of a water pump. The fibrils of the 3 mg of oxycellulose gathered on the filter and looked like a little disc. The disc was taken off the filter, placed on a spot plate and on this little disc the metals were identified by sensitive spot tests.[3] If there were several metal contaminants in the solution, we identified them by placing the disc in the middle of a filter paper on the Weisz ring oven,[4] where the metals were eluted, separated and tested. By the simple method described above, the dilution limits of the reactions were greatly increased, namely to pD 9.

Copper, nickel and zinc, bound as cyanide complexes in very dilute solutions, could not be identified by direct sensitive spot tests. By placing oxycellulose fibrils into the solutions and subsequent filtration, the testing of the copper, nickel and zinc ions could be successfully achieved on the oxycellulose disc.

Future work will be concerned with the quantitative collection of traces of metals, including radioactive isotopes, contaminants of water and extremely dilute solutions, some problems of complex stability and theoretical questions concerning the processes on the surface of the oxycellulose.

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Summary—For the collection and filtration of traces of several metal ions from extremely dilute solutions, a simple and fast method has been worked out using oxycellulose fibrils as a collector. pD 9 can be reached. Even metals bound in complexes can be filtered out.

Zusammenfassung—Es wurde ein Verfahren zur Anreicherung von Metallspuren aus extrem verdünnten wässrigen Lösungen ($1:10^9$) ausgearbeitet. Als Kollektor wurden Oxycellulose Fädchen verwendet: etwa 3 mg Oxycellulose für 1 l Lösung. Es konnten sogar die Metallkomponenten weniger stabiler Komplexverbindungen aus extrem verdünnten Lösungen mit dem Verfahren isoliert werden.

Résumé—Les auteurs suggèrent une méthode simple et rapide pour recueillir et filtrer des traces de métaux lourds, à partir de solutions extrêmenent diluées, en utilisant l'oxycellulose comme collecteur.

On peut atteindre pD = 9. Même les métaux complexés peuvent être séparés par filtration.

REFERENCES

[1] E. Schulek, Zs. Remport-Horváth and J. Laszlovszky, *Mikrochim. Acta*, 1961, 64.
[2] E. Ott, H. M. Spurlin, *Cellulose and Cellulose Derivatives Part* 1., *High Polymers Volume V.* Interscience Publishers, New York, 1954.
[3] F.Feigl, *Spot Tests in Inorganic Analysis.* Elsevier, Amsterdam, 1954.
[4] H. Weisz, *Microanalysis by the Ring Oven Technique.* Pergamon Press, Oxford, 1961.

Determination of fluothane and its isomer by means of infrared spectrophotometry

(*Received* 29 *November* 1961. *Accepted* 22 *January* 1962)

FLUOTHANE (Halothane), 1,1,1-trifluoro-2-bromo-2-chloroethane (I), a modern inhalation anaesthetic with outstanding properties,[1] is normally produced in one of three ways: by high-temperature bromination of 1,1,1-trifluoro-2-chloroethane,[2,3] by high-temperature chlorination of 1,1,1-trifluoro-2-bromoethane,[2,3] or by addition of hydrogen bromide to trifluorochloroethylene[4,5] and rearrangement of the 1,1,2-trifluoro-1-bromo-2-chloroethane (II) thus formed by means of aluminium chloride.[6]

$CF_3CHClBr$	$CF_2BrCHClF$
Fluothane	"Isomer"
I	II

A simple and fast method was worked out for the filtration of the suspended oxycellulose fibrils. A sintered-glass filter stick, 5 mm in diameter, was dipped into the solution and the fibrils were collected on the filter by means of a water pump. The fibrils of the 3 mg of oxycellulose gathered on the filter and looked like a little disc. The disc was taken off the filter, placed on a spot plate and on this little disc the metals were identified by sensitive spot tests.[3] If there were several metal contaminants in the solution, we identified them by placing the disc in the middle of a filter paper on the Weisz ring oven,[4] where the metals were eluted, separated and tested. By the simple method described above, the dilution limits of the reactions were greatly increased, namely to pD 9.

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[2] E. Ott, H. M. Spurlin, *Cellulose and Cellulose Derivatives Part* 1., *High Polymers Volume V.* Interscience Publishers, New York, 1954.
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$CF_3CHClBr$	$CF_2BrCHClF$
Fluothane	"Isomer"
I	II

The last of these methods for the production of fluothane calls for the accurate estimation of both fluothane and its isomer, and especially for the determination of small amounts of the isomer in fluothane.

The analytical separation and determination of fluothane and its isomer are very difficult. Their boiling points lie very close together (50° and 52°, respectively), and other physical properties correspond very closely. Gas-liquid chromatography, using kieselguhr impregnated with silicone oil, or Celite impregnated with dinonyl phthalate, failed entirely.[7] The retention times of the pure compounds differ only very slightly, and a mixture of the two isomers gives only a single peak.

It therefore seemed desirable to investigate the infrared characteristics of both compounds. The infrared spectra of fluothane[8] and its isomer[5] have been measured using sodium chloride optics. But

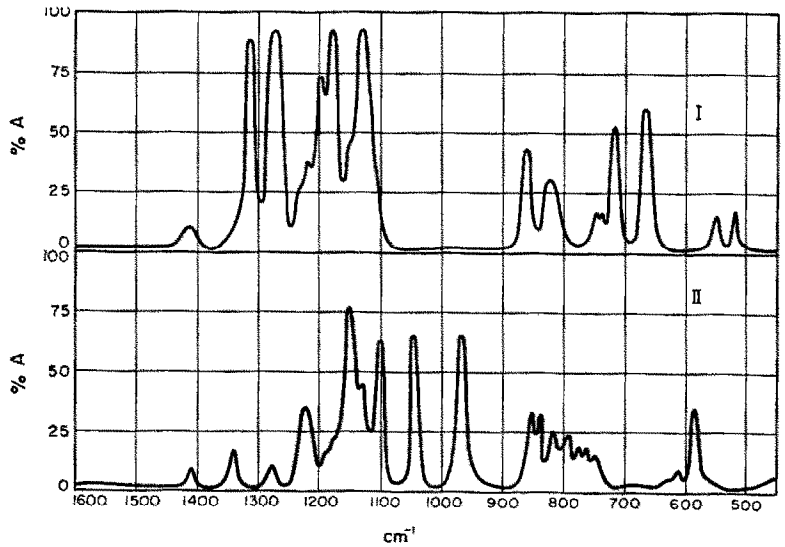


FIG. 1. Infrared spectra of fluothane and its isomer in tetrachloromethane solutions.
Curve I: Fluothane (1,1,1-trifluoro-2-bromo-2-chloroethane) (I); potassium bromide cell, c = 1%, l = 0·4 mm.
Curve II: The isomer (1,1,2-trifluoro-1-bromo-2-chloroethane) (II); potassium bromide cell, c = 0·3%, l = 0·4 mm.

as far as we can determine, no attempts have been made to record the infrared spectra at lower frequencies. Using potassium bromide optics the spectra of both compounds were recorded in the 400–700 cm^{-1} region and were found to show considerable differences, fluothane having maxima at frequencies at which its isomer does not absorb.

TABLE I. EXTINCTION COEFFICIENTS OF FLUOTHANE AND ITS ISOMER

Fluothane		Isomer	
Frequency, cm^{-1}	Extinction coeff., k	Frequency, cm^{-1}	Extinction coeff., k
520	18·0	587	81·3
552	13·0	966	218·0
665	87·0	1043	218·0
715	60·0		

$$k = \frac{A}{c(ml/10ml) \cdot d(cm)}$$

EXPERIMENTAL

The spectra were measured on a Zeiss UR-10 Infrared Spectrophotometer. Potassium bromide optics were used for measurements in the 400–700 cm^{-1} region, and sodium chloride optics for measurements at higher frequencies. Determinations were carried out in tetrachloromethane solutions in 0·04-cm potassium bromide cells. The tetrachloromethane used was of standard grade for infrared spectroscopy. The evaluation of the extinctions was carried out by the base line method.

(a) *Determination of the purity of fluothane*

The spectrum of a sample of fluothane in tetrachloromethane is recorded over the range 500–800 cm^{-1} with pure tetrachloromethane inserted in the reference beam. At 520, 552, 665, and 715 cm^{-1} extinctions are measured, and the corresponding concentrations of fluothane are read from a calibration curve constructed from measurements on fluothane solutions of known concentrations. The final value found can be taken as the arithmetic mean of the values obtained from the four frequencies.

(b) *Determination of the purity of the isomer*

The spectrum is recorded from 500 cm^{-1} to 1100 cm^{-1}. Concentrations are read from the corresponding calibration curves constructed from measurements of the absorptions at 587, 966, and 1043 cm^{-1} given by solutions of known concentrations of the isomer. The final value is taken as the arithmetic mean of the values obtained from the three independent frequencies.

(c) *Determination of the isomer in fluothane*

The crude product obtained on rearrangement of the isomer to fluothane does not, as a rule, contain more than 10% of the isomer, and usually less than 2%. The spectrum of such a sample is registered over the range 480–1100 cm^{-1}. The calculation may be based on the calibration curve of the pure isomer, or on a calibration curve constructed for mixtures of fluothane and its isomer. The latter gives more accurate results, especially when the content of the isomer in fluothane is lower than 1%. In this way it is possible to determine the content of the isomer in fluothane down to 0·1% with acceptable accuracy. By using 1·0-mm cells the sensitivity of this method could be further increased.

The accuracy of the method was checked on a series of mixtures prepared from known quantities of fluothane and its isomer. The results are given in Table II.

TABLE II. DETERMINATION OF THE AMOUNT OF THE ISOMER IN MIXTURES WITH FLUOTHANE

Concentration of the isomer in the mixture, %	Found*, %
10·0	10·06
5·0	5·02
2·0	2·07
1·0	0·98
0·5	0·52
0·2	0·22
0·1	0·11

* Average of 5 determinations.

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Summary—A new method for the determination of the purity of fluothane and its isomer, 1,1,2-trifluoro-1-bromo-2-chloroethane, is based on the evaluation of infrared spectra of both compounds. The method is particularly applicable to the determination of small amounts of the isomer in crude fluothane prepared by the rearrangement of the isomer. Using the conditions specified, the determination of as little as 0·1% of the isomer in fluothane is possible with a maximum relative error of 10%. This simple and rapid method is suitable for routine analyses.

Zusammenfassung—Eine neue analytische Methode zur Bestimmung der Reinheit von Fluothane und seinem Isomer, 1,1,2-Trifluor-1-brom-2-chloräthans, beruht auf der Verwertung von Infrarotspektren der beiden Verbindungen. Die Methode kann auch zur Bestimmung von kleinen Mengen des Isomers in rohem Fluothane, das durch Umlagerung seines Isomers bereitet wird, verwendet werden. Unter den beschriebenen Umständen ist es möglich, auch noch 0·1% des Isomers in Fluothane mit dem relativen Fehler von 10% zu bestimmen. Die Methode ist sehr einfach und wegen ihrer Schnellheit für Serienanalysen besonders zweckmässig.

Résumé—Une nouvelle méthode pour le dosage quantitatif du fluothane et son isomère, 1,1,2-trifluoro-1-bromo-2-chloroethane, utilise des spectres ultra-rouges de tous les deux composés. La méthode est aussi applicable pour détermination des petites quantités d'isomère dans fluothane, obtenu par le

rearrangement intramoléculaire de son isomère. Sous conditions décrites, des quantités si petites que 0·1% d'isomère dans fluothane peuvent être estimées avec une déviation maximale de 10% rélatif. La méthode est très simple, et pour sa rapidité, très convenable pour des analyses de routine.

REFERENCES

[1] J. Raventós, *Brit. J. Pharmacol.*, 1956, **11**, 394.
[2] A. K. Barbour, *Chem. and Ind.*, 1961,958.
[3] C. W. Suckling, *Australian Patent*, 205,979, 1955.
[4] J. D. Park, M. L. Sharrah and J. R Lacher, *J. Amer. Chem. Soc.*, 1949, **71**, 2339.
[5] R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 1954, 3747.
[6] O. Scherer and H. Kühn, *German Patent*. 1,041,937, 1957.
[7] K. Macek, *private communication.*
[8] R. Theimer and J. R. Nielsen, *J. Chem. Phys.*, 1957, **27**, 887.

The determination of nitrate in water

(*Received* 26 *January* 1962. *Accepted* 22 *February* 1962)

IN searching for a simple and reliable method suitable for the routine determination of nitrate in water, a number of colorimetric reagents including brucine and phenol disulphonic acid were investigated, but these were, in general, found to be lacking in sensitivity. Methods in which nitrate is reduced to ammonia were also investigated. Among the reagents recommended for this purpose are ferrous hydroxide and other ferrous salts, titanous chloride and Devarda's alloy. All these were tested, but in no instance could reagents be obtained which gave sufficiently low blank tests. Ferrous salts gave blank values too high to measure colorimetrically. Three samples of titanous chloride from different sources gave blanks of 0·98, 1·16 and 1·20 ppm of N. Devarda's alloy gave a blank of 0·98 ppm of N. The chromous chloride blank is usually 0·04 ppm of N.

Chromous chloride, prepared as described by Buehrer and Schupp,[1] by the reduction of potassium dichromate with zinc, was tested, and this proved to be a very effective and reliable reducing agent. The reagent as first prepared, contained a rather excessive amount of ammonia, the source of which was found to be the zinc used to prepare the reagent. The ammonia presumably comes from nitride present on the surface of the zinc, as it was found that if the zinc was boiled for a short time with hydrochloric acid and washed with water before use, a reagent could be prepared which contained only a trace of ammonia.

Distillation of a reduced water with sodium carbonate did not liberate all the ammonia formed, but good recoveries were obtained using caustic soda.

EXPERIMENTAL

Reagents

(1) *Zinc:* Granulated zinc is washed by boiling for a few minutes with hydrochloric acid diluted with an equal volume of distilled water. It is then thoroughly rinsed with distilled water.

(2) *Chromous chloride:* Boil 2 g of AnalaR potassium dichromate in a 125-ml Erlenmeyer flask with 10 ml of conc. hydrochloric acid, 5 ml of distilled water, and a large excess of purified zinc, until the colour of the solution becomes a pale blue. This takes one or two minutes. Cool the flask immediately, and cover the solution with a layer of petroleum ether (B.P. 100-120°) to inhibit oxidation. Chromous chloride reacts readily with atmospheric oxygen and the reagent must be prepared immediately before use.

(3) *Caustic Soda Solution:* Dissolve 200 g of AnalaR sodium hydroxide in distilled water and adjust the volume to 1 litre. Heat this to boiling in a Pyrex flask and add an excess of chromous chloride solution (10 ml to 20 ml may be required). Boil the solution for about 30 min, cool, filter through a Whatman No. 54 filter and adjust the volume to 1 litre.

(4) *Standard ammonium chloride solution:* Dissolve 3·8190 grams of AnalaR ammonium chloride in distilled water and adjust the volume to 1 litre. Dilute 10 ml of this solution to 1 litre to provide the working standard. One ml of the working standard is equivalent to 0·00001 g N.

rearrangement intramoléculaire de son isomère. Sous conditions décrites, des quantités si petites que 0·1% d'isomère dans fluothane peuvent être estimées avec une déviation maximale de 10% rélatif. La méthode est très simple, et pour sa rapidité, très convenable pour des analyses de routine.

REFERENCES

[1] J. Raventós, *Brit. J. Pharmacol.*, 1956, **11**, 394.
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(4) *Standard ammonium chloride solution:* Dissolve 3·8190 grams of AnalaR ammonium chloride in distilled water and adjust the volume to 1 litre. Dilute 10 ml of this solution to 1 litre to provide the working standard. One ml of the working standard is equivalent to 0·00001 g N.

Experimental details

Pipette 50 ml of water sample into a litre flask and add 200 ml of ammonia-free distilled water. Connect the flask to a distillation apparatus fitted with a dropping funnel. Heat the solution to boiling until steam emerges from the end of the condenser (the cooling water being turned off). Turn on the condenser water and collect 50 ml of distillate, test this to ensure absence of ammonia, and discard it.

Pipette 1 ml of the chromous chloride reagent into the flask and boil the solution for about 15 sec to allow thorough mixing. Add 2 ml of the 20% caustic soda solution and heat the flask until two 50-ml portions of distillate have been collected in Nessler tubes. Estimate the ammonia present colorimetrically by comparison with standard ammonium chloride solutions, using Nessler's reagent. Carry out a "blank" test as above using 250 ml of ammonia-free distilled water, 1 ml of chromous chloride and 2 ml of caustic soda solutions.

Recovery of ammonia from standard nitrate solutions

Results obtained for the analysis of forty standard nitrate solutions are shown in Table I. On the average about 2% loss has occurred.

TABLE I.—RECOVERY OF NITRATE FROM STANDARD SOLUTIONS (RESULTS EXPRESSED IN PARTS OF $N/10^6$)

Nitrate added	Nitrate found	Recovery %	Nitrate added	Nitrate found	Recovery %
0·80	·73	91	1·18	1·22	103
0·80	·73	91	1·18	1·11	94
0·80	·78	98	1·18	1·18	100
0·80	·80	100	1·18	1·24	105
0·80	·76	95	1·18	1·18	100
0·80	·76	95	1·18	1·18	100
0·80	·78	98	1·18	1·26	107
0·80	·80	100	1·18	1·09	92
0·80	·73	91	1·18	1·11	94
0·89	·89	100	1·18	1·11	94
0·89	·91	102	1·18	1·18	100
0·89	·84	94	1·58	1·49	95
0·89	·84	94	1·58	1·44	91
0·89	·87	98	1·58	1·49	95
0·89	·84	94	1·58	1·71	108
0·89	·87	98	1·58	1·64	104
0·89	·87	98	1·58	1·60	101
0·89	·87	98	1·58	1·49	95
1·11	1·11	100	1·58	1·56	99
1·18	1·29	109	1·58	1·56	99

Interference

A possible source of interference in water is albuminoid matter, but the conditions of the test are not sufficiently alkaline to cause decomposition to ammonia in any waters examined. The method, as described, does not differentiate between nitrate and nitrite in water, and if the latter is present it must be determined separately, and due allowance made in calculating the true nitrate content.

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Zusammenfassung—Eine zuverlässige und schnelle Methode zur Bestimmung von Nitrat in Wasser wird beschrieben. Nitrat wird zu Ammoniak reduziert (Chrom-II-chlorid), letzteres abdestilliert und nach Nessler kolcrimetriert.

Résumé—L'auteur décrit une méthode rapide et sûre de dosage du nitrate dans l'eau. Le nitrate est reduit en ammoniac à l'aide d'une solution de chlorure chromeux l'ammoniac produit est chassé par distillation, puis dosé par colorimétrie avec le réactif de Nessler.

REFERENCE

[1] T. F. Buehrer and O. E. Schupp, *Ind. Eng. Chem.*, 1926, **18**, 121.

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SHORT COMMUNICATIONS

Rate of hydrolysis of thiolacetic acid in basic solutions*

(*Received* 30 *May* 1961. *Accepted* 27 *September* 1961)

INTRODUCTION

THIOACETAMIDE has been used as a reagent for the precipitation of metal sulphides. Recently, there has been a great deal of interest in the reaction rates and reaction mechanisms of many metal ions with this reagent.[1-6] Hydrolysis of thioacetamide in acid and in alkaline solutions as well as in buffer systems[1,7-9] has been investigated.

Butler, Peters and Swift[8] noted that in alkaline solution, thioacetamide hydrolyses rapidly to yield the thiolacetate ion and ammonia, and that the subsequent conversion of the thiolacetate ion to produce the sulphide ion proceeds much more slowly. The rate of the latter was determined indirectly using thioacetamide as the starting material.

Rosenthal and Taylor[9] found supporting evidence that thiolacetic acid is an intermediate in the hydrolysis of thioacetamide in both acid and alkaline solutions.

The reactions of thiolacetic acid with some metal ions are known. Danziger[10] suggested that a compound is formed with cobalt, and Gutzeit[11] has shown that ammonium thiolacetate reacts with lead in cold hydrochloric acid solution to give a red precipitate of the sulphochloride which is transformed on heating into lead sulphide. Heap *et al.* obtained plumbous thiolacetate by heating tetraethyl lead and thiolacetic acid in the presence of silica gel.[12] Schiff and Tarugi recommend the use of a slightly ammoniacal solution of ammonium thiolacetate for precipitation of metal sulphide.[13] In this laboratory, preliminary investigations have shown that complex formation occurs between thiolacetic acid and salts of lead and tin. These compounds are the subject of investigations now in progress.

It was felt that before clarifying the role played by thiolacetic acid as an intermediate in the reactions of thioacetamide with metal ions, a more complete study of the properties of thiolacetic acid was necessary. Swift's value for the rate of hydrolysis of thiolacetic acid, obtained by an indirect method, is subject to question because of the assumptions made. Therefore, the rate of hydrolysis of thiolacetic acid was determined directly.

EXPERIMENTAL

Reagents

Thiolacetic acid: Eastman (practical grade), was distilled at 87-88°, and infrared spectra run at periodic intervals showed that the acid was stable for reasonable periods of time. Solutions (0·1*M*) were prepared from freshly distilled material.

Sodium hydroxide solutions: Standardised with potassium acid phthalate.

Sodium perchlorate solutions: Standardised gravimetrically with potassium chloride.

Reagent grade chemicals were used in the preparation of all solutions. For the infrared studies of thiolacetic acid, spectral grade *carbon tetrachloride* was employed as the solvent.

Apparatus

Infrared measurements were made with a Perkin-Elmer, Model 21, double beam spectrophotometer equipped with sodium chloride optics.

The ultraviolet spectrum was initially determined on a Perkin-Elmer Spectracord, Model 4000. A Beckman, Model DU, quartz spectrophotometer with a hydrogen discharge lamp and 1-cm quartz cells was also used.

The reaction vessel for the rate studies was a 38- × 200-mm test-tube with a two-hole rubber stopper.

* This investigation was supported by a U.S. Atomic Energy Commission Grant, Contract No. AT(30-1)906.

Procedure

Spectrophotometry: Solutions of thiolacetic acid, 10^{-4} *M*, were prepared, and each was adjusted with sodium hydroxide or hydrochloric acid to give a pH in the range 4·5-11·0. The ultraviolet spectrum of each solution was obtained, and the relationship between concentration of the acid and optical density was determined at 243 mμ. For the infrared spectrum, a ~ 5% (by weight) solution of thiolacetic acid in carbon tetrachloride was found to be satisfactory.

Rate measurements: Solutions for each experiment were prepared from distilled water and standard stock solutions of sodium hydroxide and sodium perchlorate. Each solution was preheated in the reaction tube to a temperature of 90° ± 1° and the thiolacetic acid solution was then pipetted into the vessel.

At timed intervals, ranging from 10-160 min after initiating reaction, samples of the solution were removed from the reaction tube and transferred to 50-ml volumetric flasks. After dilution, the thiolacetic acid concentration was determined spectrophotometrically.

RESULTS AND DISCUSSION

Spectrophotometry

The infrared spectrum for a solution of thiolacetic acid in carbon tetrachloride is shown in Table I and is compared with the values and assignments of Sheppard[14] for thiolacetic acid as a vapour. The results are essentially identical.

TABLE I.—INFRARED ANALYSIS OF THIOLACETIC ACID

Assignment*		Literature values*(vapour)		Observed (liquid)	
CH_3	Stretch	2920 cm^{-1}	(m)		
SH	Stretch	2550	(m)	2550 cm^{-1}	(m)
C=O	Stretch	1696	(vs)	1690	(vs)
CH_3	Asymm. deform.	1415	(m)	1410	(m)
CH_3	Symm. deform.	1352	(s)	1350	(s)
CH_3	In-plane wag	1126	(s)	1120	(s)
C—C	Stretch	993	(s)	990	(s)
SH	Deform.	838	(m)	830	(m)

* Sheppard[14]

Crouch[15] attributes the absence of bands at 3400 cm^{-1} and 960 cm^{-1} to the absence of OH and C=S groups respectively, indicating that the acid has the thiol structure, $CH_3.CO.SH$, rather than the thio structure, $CH_3.CS.OH$. It is also worthy of note that thiolacetic acid, upon standing for several days does not show any change in the infrared spectrum.

In the ultraviolet region Rosenthal and Taylor[9] observed a shift in the maximum for very acidic or very basic thiolacetic acid solutions. However, for the pH range 4·5-11·0, the maximum absorbance remained at 243 mμ.

Rate measurements

Experiments were conducted with various initial thiolacetic acid and sodium hydroxide concentrations. These concentrations were chosen in order to obtain information on conditions comparable to those described in the literature[8] for the rate of hydrolysis of thiolacetic acid using thioacetamide as the starting material. The results are shown in Table II.

TABLE II.—SECOND-ORDER RATE CONSTANT FOR THE HYDROLYSIS OF THIOLACETIC ACID IN ALKALINE SOLUTION AT 90°.

Series	Init. conc., *mole/litre* NaOH	CH_3COSH	No. of detns.	k′, *litre/mole/min*
1	0·10	0.03	20	0·011
2	0·10	0·02	3	0·011
3	0·08	0·02	3	0·010
4	0·30	0·02	3	0·010
			Weighted Average	0·010 ± ·0015

The ionic strength for all experiments was 0·30; all initial concentrations are for 25°.

Order of reaction and calculation of velocity constant

For the reaction

$$A + B \ldots \xrightarrow{k'} \text{products}$$

the second-order rate constant was calculated from the integrated form of the rate equation[16]:

$$\ln \frac{C_A}{C_B} = (C_{A_0} - C_B)\, k't + \ln \frac{C_{A_0}}{C_B}$$

when A represents thiolacetic acid and B is the hydroxyl ion. C_{A_0} and C_{B_0} are initial concentrations of thiolacetic acid and hydroxyl ion respectively at time, $t = 0$.

The logarithmic plot of the ratio $\frac{C_A}{C_B}$ versus time gives a straight line whose slope is equal to $[C_{A_0} - C_{B_0}]\, k'$. The value of k′ was calculated from this expression and the second-order velocity constant is found to be 0·010 ± 0·0015 litre mole^{-1} min.$^{-1}$ at 90°.

Temperature dependence of hydrolysis of thiolacetate

A series of experiments was performed to determine the change in the rate of hydrolysis of thiolacetate over the range 70°-90°. The reaction solutions were initially 0·03*M* in thiolacetate and 0.010*M* in sodium hydroxide; the ionic strength of the solution was adjusted to 0·030 with sodium perchlorate. In Table III are shown the values of the second-order velocity constant, k′, obtained for the temperatures stated. The energy of activation was calculated from a plot of $-\log k'$ *vs* $\frac{1}{T}$ and was found to be 23 ± 2 kcal per mole.

TABLE III.—VARIATION WITH TEMPERATURE OF SECOND-ORDER RATE CONSTANT FOR HYDROLYSIS OF THIOLACETIC ACID IN ALKALINE SOLUTIONS

Temperature, °C	Second-order rate constant, k′, *litre mole^{-1} min^{-1}*
70	0·0020
80	0·0044
90	0·010

The values for the second-order rate constants are about one-half those reported by Butler[8] while the activation energy was found to be approximately the same. Butler used thioacetamide as the starting material and although the similarity in activation energies indicates that the same reaction may be involved in both cases, the rate constants are sufficiently different to warrant consideration.

Analytical considerations

These experiments show that thiolacetic acid hydrolysis is slower than previously thought. Further considerations of this discrepancy in reacton rates must be made and incorporated into any proposed mechanism of thioacetamide reaction. If one assumes that the rate of hydrolysis is slower, this suggests that there might be sufficient thiolacetic acid present as the result of the breakdown of thioacetamide to be significant in forming intermediates with metal ions. Apparently the reaction of thioacetamide with different metals does not show any significant trends which could result from the fact that complex formation between thiolacetic acid and metal ions has been neglected.

Preliminary investigations in this laboratory have shown that lead and tin complex-formation occurs with thiolacetic acid. The complexes have been isolated and studied, and the work has been expanded to include various cations.

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Summary—The infrared spectrum obtained for thiolacetic acid dissolved in carbon tetrachloride has been found to be similar to that of the vapour phase. The ultraviolet spectrum had been determined in solutions of varying pH (4·5-11·0) and it has been found that the spectral curve as a function of acidity remains unchanged. The molar extinction coefficient at 243 mμ for thiolacetic acid has been calculated to be 6666 litre mole^{-1}cm^{-1}. The rate of hydrolysis of thiolacetic acid in alkaline solutions is found to be first-order with respect to the thiolacetate and hydroxyl ion concentrations. The second-order rate constant is 0·010 ± 0·0015 litre mole^{-1} min^{-1} at 90°. The energy of activation has been calculated to be 23 ± 2 kcal per mole from 70° to 90°.

Zusammenfassung—Das Infrarotspektrum von in Tetrachlorkohlenstoff gelöster Thioessigsäure wird als ähnlich dem der Gasphase gefunden. Das UV-Spektrum in Lösungen verschiedenen pH-Wertes (4·5-11·0) wurde studiert und es wurde gefunden, dass die Kurven unabhängig vom Säuregrad sind. Der molare Extinktionskoeffizient bei 243 mμ wurde zu 6666 l.mol^{-1}.cm^{-1} berechnet. Die Geschwindigkeit der Hydrolyse wurde bestimmt. Es wurde gefunden, dass die Reaktion in Bezug auf Thioessigsäure und Hydroxylionen erster Ordnung ist. Die Geschwindigkeitskonstante der Reaktion zweiter Ordnung ist 0·01 ± 0·0015 l.mol^{-1}.min^{-1} bei 90°C. Die Altivierungsenergie wurde zu 23 ± 2 kcal per Mol (70 — 90°C) berechnet.

Résumé—Le spectre infra-rouge obtenu pour l'acide thiolacétique dissous dans le tétrachlorure de carbone est trouvé semblable à celui de la phase vapeur.

Le spectre ultra-violet a été déterminé dans des solutions de différents pH(4, 5-11,0); les auteurs ont trouvé que la courbe spectrale en fonction de l'acidité restait inchangée. Le coefficient d'extinction molaire à 243 mμ pour l'acide thiolacétique a été calculé : 6666 litres molé$^{-1}$ cm^{-1}.

La vitesse d'hydrolyse de l'acide thiolacétique en solution alcaline a été déterminée : elle est du premier ordre par rapport aux concentrations du thiolacétate et de l'ion hydroxyle. La constante de vitesse du deuxieme ordre est 0,010 ± 0,0015 litre molé$^{-1}$min^{-1}. à 90°C. L'énergie d'activation calculée est 23 ± 2 kcal. par mole de 70 à 90°C.

REFERENCES

[1] E. H. Swift and E. A. Butler, *Analyt. Chem.*, 1956, **28**, 146.
[2] E. A. Butler and E. H. Swift, *ibid.*, 1957, **29**, 419.
[3] D. F. Bowersox and E. H. Swift, *ibid.*, 1958, **30**, 1288.
[4] E. H. Swift and F. G. Anson, *Talanta*, 1960, **3**, 296.
[5] D. F. Bowersox, D. M. Smith and E. H. Swift, *ibid.*, 1960, **3**, 282.
[6] D. Rosenthal and T. I. Taylor, *J. Amer. Chem. Soc.*, 1960, **82**, 4169.
[7] D. G. Peters and E. H. Swift, *Talanta*, 1958, **1**, 30.
[8] E. A. Butler, D. G. Peters and E. H. Swift, *Analyt. Chem.*, 1958, **30**, 1379.
[9] D. Rosenthal and T. I. Taylor, *J. Amer. Chem. Soc.*, 1957, **79**, 2684.
[10] J. L. Danziger, *ibid.*, 1902, **24**, 578.
[11] G. Gutzeit, *Helv. Chim. Acta*, 1929, **12**, 713, 829.
[12] R. Heap, B. C. Saunders and G. J. Stacy, *J. Chem. Soc.*, 1951. 658.
[13] R. Schiff and N. Tarugi, *Z. analyt. Chem.*, 1895, **34**, 456.
[14] N. Sheppard, *Trans. Faraday Soc.*, 1949, **45**, 693.
[15] W. W. Crouch, *J. Amer. Chem. Soc.*, 1952, **74**, 2926.
[16] S. W. Benson. *The Foundations of Chemical Kinetics.* McGraw-Hill Book Company, Inc., New York, 1960, p. 18.

Spot test for bi- and quadrivalent sulphur in organic compounds based on reduction with Raney alloy*

(*Received* 25 *January* 1962. *Accepted* 22 *February* 1962)

In a previous paper[1] it has been reported that Raney alloy and caustic alkali is a much more reactive reductant than Devarda alloy. For instance, if alkaline solutions of aromatic sulphonic acids or pyridine (or pyridinesulphonic acids) are heated with these alloys, reductive separation of the SO_3H group or hydrogenation to piperidine is accomplished only by the Raney alloy. The latter consists

* Translated by Ralph E. Oesper, University of Cincinnati, Ohio, U.S.A.

Summary—The infrared spectrum obtained for thiolacetic acid dissolved in carbon tetrachloride has been found to be similar to that of the vapour phase. The ultraviolet spectrum had been determined in solutions of varying pH (4·5-11·0) and it has been found that the spectral curve as a function of acidity remains unchanged. The molar extinction coefficient at 243 mμ for thiolacetic acid has been calculated to be 6666 litre mole^{-1}cm^{-1}. The rate of hydrolysis of thiolacetic acid in alkaline solutions is found to be first-order with respect to the thiolacetate and hydroxyl ion concentrations. The second-order rate constant is 0·010 ± 0·0015 litre mole^{-1} min^{-1} at 90°. The energy of activation has been calculated to be 23 ± 2 kcal per mole from 70° to 90°.

Zusammenfassung—Das Infrarotspektrum von in Tetrachlorkohlenstoff gelöster Thioessigsäure wird als ähnlich dem der Gasphase gefunden. Das UV-Spektrum in Lösungen verschiedenen pH-Wertes (4·5-11·0) wurde studiert und es wurde gefunden, dass die Kurven unabhängig vom Säuregrad sind. Der molare Extinktionskoeffizient bei 243 mμ wurde zu 6666 l.mol^{-1}.cm^{-1} berechnet. Die Geschwindigkeit der Hydrolyse wurde bestimmt. Es wurde gefunden, dass die Reaktion in Bezug auf Thioessigsäure und Hydroxylionen erster Ordnung ist. Die Geschwindigkeitskonstante der Reaktion zweiter Ordnung ist 0·01 ± 0·0015 l.mol^{-1}.min^{-1} bei 90°C. Die Altivierungsenergie wurde zu 23 ± 2 kcal per Mol (70 — 90°C) berechnet.

Résumé—Le spectre infra-rouge obtenu pour l'acide thiolacétique dissous dans le tétrachlorure de carbone est trouvé semblable à celui de la phase vapeur.

Le spectre ultra-violet a été déterminé dans des solutions de différents pH(4, 5-11,0); les auteurs ont trouvé que la courbe spectrale en fonction de l'acidité restait inchangée. Le coefficient d'extinction molaire à 243 mμ pour l'acide thiolacétique a été calculé : 6666 litres molé$^{-1}$ cm^{-1}.

La vitesse d'hydrolyse de l'acide thiolacétique en solution alcaline a été déterminée : elle est du premier ordre par rapport aux concentrations du thiolacétate et de l'ion hydroxyle. La constante de vitesse du deuxieme ordre est 0,010 ± 0,0015 litre molé$^{-1}$min^{-1}. à 90°C. L'énergie d'activation calculée est 23 ± 2 kcal. par mole de 70 à 90°C.

REFERENCES

[1] E. H. Swift and E. A. Butler, *Analyt. Chem.*, 1956, **28**, 146.
[2] E. A. Butler and E. H. Swift, *ibid.*, 1957, **29**, 419.
[3] D. F. Bowersox and E. H. Swift, *ibid.*, 1958, **30**, 1288.
[4] E. H. Swift and F. G. Anson, *Talanta*, 1960, **3**, 296.
[5] D. F. Bowersox, D. M. Smith and E. H. Swift, *ibid.*, 1960, **3**, 282.
[6] D. Rosenthal and T. I. Taylor, *J. Amer. Chem. Soc.*, 1960, **82**, 4169.
[7] D. G. Peters and E. H. Swift, *Talanta*, 1958, **1**, 30.
[8] E. A. Butler, D. G. Peters and E. H. Swift, *Analyt. Chem.*, 1958, **30**, 1379.
[9] D. Rosenthal and T. I. Taylor, *J. Amer. Chem. Soc.*, 1957, **79**, 2684.
[10] J. L. Danziger, *ibid.*, 1902, **24**, 578.
[11] G. Gutzeit, *Helv. Chim. Acta*, 1929, **12**, 713, 829.
[12] R. Heap, B. C. Saunders and G. J. Stacy, *J. Chem. Soc.*, 1951. 658.
[13] R. Schiff and N. Tarugi, *Z. analyt. Chem.*, 1895, **34**, 456.
[14] N. Sheppard, *Trans. Faraday Soc.*, 1949, **45**, 693.
[15] W. W. Crouch, *J. Amer. Chem. Soc.*, 1952, **74**, 2926.
[16] S. W. Benson. *The Foundations of Chemical Kinetics.* McGraw-Hill Book Company, Inc., New York, 1960, p. 18.

Spot test for bi- and quadrivalent sulphur in organic compounds based on reduction with Raney alloy*

(*Received* 25 *January* 1962. *Accepted* 22 *February* 1962)

In a previous paper[1] it has been reported that Raney alloy and caustic alkali is a much more reactive reductant than Devarda alloy. For instance, if alkaline solutions of aromatic sulphonic acids or pyridine (or pyridinesulphonic acids) are heated with these alloys, reductive separation of the SO_3H group or hydrogenation to piperidine is accomplished only by the Raney alloy. The latter consists

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of 50% Ni and 50% Al. Tests for aromatic sulphonic acids and their derivatives, and also a test for pyridine (and pyridinesulphonic acids) have been based on this finding.[3] The reason that reductions which fail with Devarda alloy can be accomplished in alkaline media through Raney alloy is that the hydrogen liberated during the formation of the alkali aluminate is partly retained by metallic nickel as hydride, so that so-called Raney nickel results. Accordingly, metallic nickel or, more correctly, the formation of nickel hydride, catalytically hastens reductions in alkaline media. It seemed logical to assume that solution of Raney alloy in hydrochloric acid with initial production of aluminium chloride and hydrogen would likewise result in the formation of nickel hydride through union of the hydrogen with the slightly soluble metallic nickel. If this were the case, it should be possible to accomplish reductions which do not succeed with the hydrogen obtained from Devarda alloy and acid. A necessary condition would be that the speed of formation of the hydride and of reduction are greater than the solution velocity of the Raney alloy and the Raney nickel formed from this alloy. This is the case with methylene blue, as shown by the following experiment. If equal parts of a 5% hydrochloric acid solution of the dyestuff are treated with several cg of (a) Raney alloy, or (b) Devarda alloy, hydrogen sulphide is produced only by the Raney alloy, as revealed by the blackening of lead acetate paper. This effect may be observed even with very dilute solutions of the dyestuff.

Since it is well known that methylene blue is very quickly reduced to the leuco compound by hydrogen, the production of hydrogen sulphide on warming with Raney alloy demonstrates that nickel hydride in acid media can bring about a reductive cleavage of the bivalent sulphur from the leuco compound. This is in conformity with the additional finding that open and cyclic thioethers, as well as aliphatic and aromatic disulphides, behave in this same manner when they are warmed with Raney alloy and acid. This production of hydrogen sulphide leads to a means of detecting compounds of these types hitherto lacking. It should be noted that thiols and thioketones are reductively cleaved by "nascent" hydrogen (hence by Devarda alloy and acid) with production of hydrogen sulphide. Similarly, sulphoxides and sulphinic acids yield hydrogen sulphide when warmed with Raney alloy and acid, whereas sulphonic acids and their derivatives, as well as sulphones, *i.e.*, compounds containing sexavalent sulphur, remain unaltered. Accordingly, reduction with Raney alloy provides a reliable preliminary test for bi- and quadrivalent sulphur in organic compounds, even in the presence of sexavalent sulphur.

The reductive cleavage of organic sulphides by Raney alloy in hydrochloric acid solution, with participation of nickel hydride (Raney nickel) as hydrogen donor, can be formulated

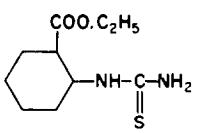
$$[R(Ar)]_2S + 4NiH + 8HCl \rightarrow 2R(Ar)H + H_2S + 4NiCl_2 + 8H^\circ$$

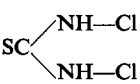
Analogous equations can be written for disulphides and other aliphatic and aromatic compounds containing bi- and quadrivalent sulphur.

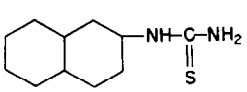
The test described here provides a means of detecting sulphur dyes, *e.g.*, thiazine dyes in the presence of dyes which contain sulphonic groups, *i.e.*, sexavalent sulphur. This test may also be applied in the differentiation of sulpha compounds (sulpha drugs) since only those which contain bivalent sulphur react with Raney alloy and acid to yield hydrogen sulphide. Such dyestuffs and sulpha compounds were among the compounds tested by us.

Procedure: The test is conducted in a micro test-tube. A little of the solid test material, or 1 drop of its solution, is treated with several cg of Raney alloy and 1–2 drops of concentrated hydrochloric acid. After the vigorous evolution of hydrogen has subsided, the open end of the test-tube is covered with a piece of lead acetate paper. The test-tube is then placed in a water bath at 80° and then at 100°. A positive response is shown by the development of a brown or black stain on the reagent paper.

Limits of identification:

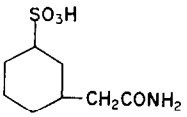
2·5 μg *o*-carboxyphenylthiourea ethyl ester, 

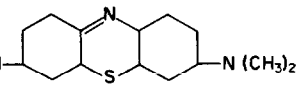
2·5 μg dichlorothiourea, 

2·5 μg 1-naphthylthiourea, 

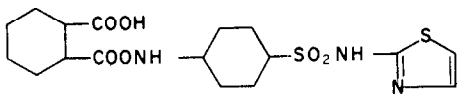
5 μg 4,4′-bis(dimethylamino)thiobenzophenone, $[(CH_3)_2NC_6H_5]_2CS$

2·5 μg thiocarbanilide, C_6H_5—NH—CS—NH—C_6H_5

2·5 μg 3-acetamino-4-methoxy-benzolsulphinic acid, 

2·5 μg methylene blue, 

2·5 μg 1-cystine, [—$SCH_2CH(NH_2)COOH$]$_2$

3 μg phthalyl sulphathiazole, 

5 μg dithio-oxamide, $NH_2CSCSNH_2$

1 μg benzene sulphinic acid, sodium salt, $C_6H_5SO_2Na$

5 μg *p*-toluene sulphinic acid, sodium salt, $CH_3C_6H_4SO_2Na$

Acknowledgement—We gratefully acknowledge the financial support provided by the Conselho Nacional de pesquisas.

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Ministerio das Minas e Energia
Rio de Janeiro, Brazil

FRITZ FEIGL
DORA HAGUENAUER-CASTRO

Summary—Organic compounds containing bi- or quadrivalent sulphur are cleaved when warmed with Raney alloy and hydrochloric acid, and yield hydrogen sulphide. This has been made the basis of a preliminary test for compounds of this kind. Identification limits from 1–5 μg are obtained in spot test analyses.

Zusammenfassung—Organische Verbindungen die 2-oder 4-wertigen Schwefel enthalten, spalten bei Erwärmung mit Raney Legierung und Salzsäure Schwefelwasserstoff ab. Darauf lässt sich ein Vorprobe auf hierhergehörige Verbindungen begründen. In der Arbeitsweise der Tüpfelanalyse werden Erfassungsgrenzen vom 1-5 ug erhalten.

Résumé—Les composés organiques contenant du soufre aux degrés d'oxydation +2 ou +4 sont clivés lorsqu'ils sont chauffés avec l'alliage Raney et de l'acide chlorhydrique, et forment de l'acide sulfhydrique. Cette découverte est la base d'une recherche préliminaire des composés de cette espèce. Des limites d'identification de 1–5 μg ont été obtenues au moyen de la technique d'essai par touches.

REFERENCES

[1] F. Feigl, *Angew. Chem.*, 1961, **73**, 113.
[2] *Idem*, *Analyt. Chem.*, 1961, **33**, 1118.

Talanta, 1962, Vol. 9, p. 543. Pergamon Press Ltd. Printed in Northern Ireland

EDITORIAL NOTES

1. Starting in January, 1963, all books submitted to TALANTA will be listed under the heading of "Publications Received". The number of actual book reviews published will, however, be substantially reduced.

2. The attention of contributors is drawn to the fact that papers submitted for publication in TALANTA should essentially be new publications. The submission of a paper to the Editor-in-Chief is held to imply that it has not previously been published in any major language, that it is not under consideration for publication elsewhere and that, if accepted for publication, it will not be published elsewhere in the same form in any major language without the written consent of the Editor-in-Chief.

3. In response to request from subscribers, the volume indexes for TALANTA in future years will be included as a separate inset and not bound in with the issue in which they appear.

Talanta, 1962, Vol. 9, pp. 545 to 546. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

AUSTRALIA

February 1963: **First Australian Conference on Electrochemistry:** *Royal Australian Chemical Institute, University of Tasmania and University of N.S.W.* Sydney and Hobart.

The following topics are among those to be discussed: thermodynamics of electrolytes, electroanalytical methods, electrode processes, fused salts and non-aqueous electrochemistry.

Further details are available from Dr. F. GUTMANN, Department of Physical Chemistry, University of N.S.W., P.O. Box 1, Kensington, N.S.W., Australia.

CZECHOSLOVAKIA

Monday-Tuesday 30–31 *July* 1962: **Meeting of I.U.P.A.C. Division for Oils and Fats.** Prague.

UNITED KINGDOM

Thursday–Friday 28–29 *June* 1962: Symposium on **Instrument Techniques in Industry and Research:** *Society for Analytical Chemistry, Scottish and North of England Sections.* Queen's University of Belfast, N. Ireland.

The following papers are among those to be presented:

Analytical Uses of the Flame Emission Spectra of Lead and Titanium.	C. L. CHAKRABARTI, R. J. MAGEE and C. L. WILSON
Quantitative Gas-Liquid Chromatography in the Routine and Research Laboratory.	A. F. WILLIAMS
Applications of Vapour Phase Infrared Spectroscopy to the Functional Group Analysis of Propoxy- and Butoxy-Compounds by Modified Zeisel Reactions.	D. M. W. ANDERSON

Thursday–Friday 5–6 *July* 1962: Symposium on **Spectroscopy in the Metallurgical Industry:** *Institute of Physics and Physical Society, Spectroscopy Group* and *British Non-Ferrous Metals Research Association* and *British Iron and Steel Research Association.* Buxton, Derbyshire.

Further details may be obtained from the Administration Assistant, Institute of Physics and Physical Society, 47, Belgrave Square, London, S.W.1

Thursday–Saturday 20–22 *September* 1962: Joint Symposium on **Standardisation in Non-Destructive Testing:** *Non-Destructive Testing Society of Great Britain* and *Institution of Production Engineering. Old Swan Hotel,* Harrogate.

Further details may be obtained from the Secretary, Institution of Production Engineering, 10, Chesterfield Street, Mayfair, London, W.1.

Wednesday–Friday 3–5 *April* 1963: Symposium on **Soil Analysis and Its Relation to Plant Composition and Growth:** *Society of Chemical Industry, Agriculture Group:* Bristol.

Further details may be obtained from the Assistant Secretary, Society of Chemical Industry, 14, Belgrave Square, London, S.W.1.

13–17 *April* 1964: **Second International Fermentation Symposium:** Society of Chemical Industry. London.

The subjects to be discussed are classified under the following broad groups:

Instrumentation.	*Culture Maintenance and Genetics.*
Antibiotics and Other Products of Fermentation.	*Continuous Culture.*
Biochemical Engineering.	*Tissue Culture and Vaccines.*

Further details may be obtained from the Hon. Secretary, Second International Fermentation Symposium, Society of Chemical Industry, 14, Belgrave Square, London, W.1.

The following *New British Standard* is announced by **British Standards Institution:**

B.S. 3477: 1962: Method for the determination of oils, fats and waxes in cotton. This describes a method for the removal and determination of oil, fat or fatty acid, in raw, scoured, and bleached cotton, and in cotton containing a stated variety of ingredients added as size or finish. Certain materials containing oxidised unsaturated oils, waterproofing or softening preparations, rot-proofing agents and synthetic resins are excluded. (Price 3s.)

The following *Revised British Standard* is announced:

B.S. 846: 1962: Burettes and bulb burettes. This specifies in Part 1, 10 sizes of burette from 1 to 100-ml capacity and in Part 2 bulb burettes of 45, 65, 85 and 105-ml capacity. It includes dimensions, tolerances on capacity, delivery times, and requirements for material, construction and graduation (Price 7s. 6d.)

The following *Amendment Slips* are announced:

B.S. 1728: Methods for the analysis of aluminium and aluminium alloys: Part 4: 1952: Zinc (polarographic method). Amendment No. 2: PD 4521.

B.S. 2728: Methods of testing plastics: Part 4: 1958: Analytical methods and viscosity in solution. Amendment No. 8: Methods 401: PD 4467.

UNITED STATES OF AMERICA

Tuesday–Friday 17–20 *July* 1962: **Second International Symposium on Fluorine Chemistry:** *American Chemical Society, Division of Industrial and Engineering Chemistry* and *Air Force Materials Central* and *University of Denver.* The Stanley Hotel, Estes Park, Colo.

The lecture programme contains the following paper of interest to analytical chemists:

Null-Point Potentiometric Determination of Fluoride.	T. A. O'DONNELL

Monday–Tuesday 6–7 *August* 1962: **Fifth Annual Rocky Mountain Spectroscopy Conference:** *Society for Applied Spectroscopy, Rocky Mountain Section.* Olin Hotel, Denver, Colo.

The conference will feature symposia on:

Medical and Biochemical Materials	*Trace Analysis*
Applications of the Vacuum Ultraviolet Region	*Mineralogical Analysis.*

Further details may be obtained from FRANCIS S. BONOMO, Denver Research Institute, University of Denver, Denver 10, Colo.

Monday 29 *October* 1962: Third Informal Symposium on **Vacuum Microbalance Techniques.** Statler Hilton Hotel, Los Angeles, California.

Further details may be obtained from Dr. KLAUS BEHRNDT, Dept. 592-50, General Dynamics/ Astronautics, P.O. Box 166, San Diego 12, Calif.

ERRATA—Volume 9

Page 225: the author in reference 4 should read J. S. HETMAN.

Page 405, line 12: for 1933 read 1923.

Talanta, 1962, Vol. 9, p 547. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

The determination of thallium in urine: M. ARIEL and D. BACH. (2 *April* 1962)

Quantitative treatment of exchange equilibria involving complexans—I: General consideration and scope of applications in analytical chemistry: GENKICHI NADAGAWA and MOTOHARU TANAKA. (3 *April* 1962)

Photometric determination of uranium in calcium fluoride with 1-(2-pyridylazo)-2-naphthol (pan) using 1,2-diaminocyclohexane-tetra-acetic acid as masking agent: K. L. CHENG. (6 *April* 1962).

Thermogravimetry of some uranium^{VI} 8-hydroxyquinolates: JON BORDNER and LOUIS GORDON. (6 *April* 1962)

Identification of polyatomic anions by infrared spectroscopy: F. R. HABA and C. L. WILSON. (27 *April* 1962)

Sub-micro determination of iron in organic materials: T. R. F. W. FENNELL and J. R. WEBB. (27 *April* 1962)

The separation and determination of microgram or sub-microgram quantities of gold in copper: The use of mercury as a collector: ATSUSHI MIZUIKE. (27 *April* 1962)

Quantitative treatment of exchange equilibria involving complexans—II: Polarographic determination of calcium in the presence of magnesium: GENKICHI NAKAGAWA and MOTOHARU TANAKA. (27 *April* 1962)

Potentiometric determination of vanadium^{IV} with cerium^{IV} sulphate at the room temperature. Simultaneous differential potentiometric titration of iron^{II} and vanadium^{IV} at room temperature: L. S. A. DIKSHITULU and G. GOPALA RAO. (27 April 1962)

Resacetophenone phenylhydrazone as a reagent for the estimation of copper: P. UMAPATHY and N. APPALA RAJU. (30 April 1962)

Talanta, 1962, Vol. 9, pp. 549 to 557. Pergamon Press Ltd. Printed in Northern Ireland

SOME CONSIDERATIONS ON MASKING EFFECTIVENESS

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(*Received* 23 *November* 1961. *Accepted* 20 *February* 1962)

Summary—A new term, the masking coefficient, has been derived and introduced in analytical considerations involving masking of precipitation reactions. The masking coefficient is expressed by an equation:

$$pM' = \frac{1}{j+i}[pS - i\log(j/i)] - \frac{j}{j+i}\log\alpha_M - \frac{i}{j+i}\log\alpha_A$$

where the first term is related only to the properties of the precipitate, the second to masking of the cation, and the last to masking of the anion. If suitable diagrams have been prepared for calculating the "side reaction coefficients"—log α_M and log α_A—all calculations can be easily performed. The utility of the masking coefficient criterion to predict whether masking or precipitation occurs has been confirmed experimentally. Some examples of calculation of the masking coefficient for well known analytical reactions are given.

THE immense development of analytical chemistry has demanded the introduction of many new selective reagents and so-called masking agents, which may greatly improve the selectivity and specificity of analytical reactions.[1,4] Recently Cheng[2] has presented an extensive study on the use of some masking agents, especially ethylenediaminetetra-acetic acid (EDTA) combined with many inorganic and organic precipitants.

The correct choice of a suitable masking agent for a given principal reaction (as called by Cheng[2]), is very often solved experimentally by trying a sufficiently large set of available reagents. This procedure is rapid, but does not provide any instant indication of how effective the process of masking is, especially when compared with other masking reactions. Evaluation of detailed conditions for the equilibrium position or its shift is obviously possible on the basis of a knowledge of corresponding equilibrium constants. This will give accurate results, but the exact mathematical treatment is, in most cases, rather long and complicated.

The use of conditional constants[3,5] offers some advantages if they are used in calculation instead of the thermodynamic constants. Nevertheless it would be worthwhile to have a general expression for simple evaluation of the equilibrium position in systems containing metal ion, precipitating and masking agents.

Recently Cheng[2] has attempted to do this by introducing the term "Selectivity Ratio" (S.R.), which he has defined as:

$$\text{S.R.} = (pM_p)^2/pM_m$$

where pM_p and pM_m denote the negative logarithm of the metal ion concentrations dissociated from the metal principal agent complex (or precipitate) and metal masking agent, respectively.

Calculation of Cheng's Selectivity Ratio should give for any system an indication whether the principal or the masking reaction will proceed. The limiting value, according to Cheng, is approximately equal to 7·0. If S.R. is greater than 7·0 the

precipitate will be obtained, but if it is smaller then masking is more effective. Nevertheless, a more careful inspection of S.R. indicated some disadvantages of this procedure. Firstly, S.R. is not directly related to any physical magnitude and represents a rather artificially formed term. Thus it is not possible to give in any general way an intermediate range, where reasonable changes of reagent concentrations may shift an equilibrium in any direction. Furthermore, pM_m values correspond to a very special system, containing a $1M$ concentration of metal complex and stoicheiometrically equal concentrations of metal ion and free ligand. The use of conditional constants, already mentioned, is not readily applicable in S.R. calculation, but if conditional constants have been used the simplicity of S.R. calculations suffers seriously. In spite of the fact that S.R. in some instances gives experimentally verified results, cases can be found where its indications are false. This occurs, for example, in the masking of silver chloride or silver ferricyanide by ammonia, and of silver ferrocyanide by potassium cyanide. Those erroneous indications appear especially in systems for which pM_p and pM_m values do not differ significantly.

Taking into account the mentioned facts it is concluded that the Selectivity Ratio method is not sufficiently accurate in many practical systems to be of analytical value. In the present paper another method of evaluation of masking effectiveness is proposed and examples are given. This treatment will be concerned with principal reactions based on precipitation and their masking by complexation.

THEORETICAL CONSIDERATIONS

Direct comparison of stability constants of complexes and solubility products of precipitates does not give any prompt indication about the position of the equilibrium in the case where reaction products have a different metal ion:complexing (or precipitating) agent ratio. The correct conclusion can be drawn when the concentration of metal ion is calculated from the amount of ions produced from salt dissociation in the absence of any common ions. In the general case of a salt M_jA_i with a solubility product S, the metal concentration is given by:

$$[M] = \sqrt[j+i]{S(j/i)^i} \tag{1}$$

or in a logarithmic form:

$$pM = \frac{1}{j+i}[pS - i\log(j/i)] \tag{2}$$

The presence of a masking agent increases the solubility of this salt when complexing occurs. To calculate the solubility it is necessary to use in this case conditional constants instead of thermodynamic constants. The relationship between the thermodynamic and conditional constants is given by:

$$S'_{M_jA_i} = S \cdot \alpha_M^j \cdot \alpha_A^i \tag{3}$$

where $S'_{M_jA_i}$ represents the conditional solubility product, and α_M and α_A are the side reaction coefficients for the cation and anion of the salt M_jA_i, respectively.

By the term conditional solubility product, S', an expression is understood which in contrast to the thermodynamic solubility product, S—a function of free precipitate forming ions—is a function of total metal and precipitating agent in solution, independent of whether they exist as free ions or in the form of other species (*e.g.* complexed,

protonated, *etc.*), as long as they are in equilibrium with the precipitate. Thus

$$S' = [M']^j[A']^i.$$

On the other hand, the side reaction coefficients, α_M and α_A, represent the ratio of the total concentration of the metal-containing, and anion-containing species (not involved in the principal reaction, in this case precipitation) to concentration of their free ions, respectively. According to these definitions

$$\alpha_M = \frac{[M']}{[M]} \quad \text{and} \quad \alpha_A = \frac{[A']}{[A]}.$$

In special cases, when a given ion undergoes only one type of reaction or when the contribution of the other reaction can be neglected, instead of $[M']$, $[A']$, *etc.* one can use analytical concentrations of these species.

Considering the process of masking, we are interested in the total concentration $[M']$ of a metal ion in equilibrium with the precipitate, but not in the actual concentration of free (hydrated) ions, and thus we can write instead of (2), a "primed" equation:

$$pM' = \frac{1}{j+i}[pS - i \log (j/i)] \tag{4}$$

From (3) and (4) we obtain a relationship between the thermodynamic solubility products and the side reaction coefficients α_M and α_A, which in fact depend on the experimental conditions of masking. Thus the total metal ion concentration equals:

$$pM' = \frac{1}{j+i}[p(S\alpha_M^j \alpha_A^i) - i \log (j/i)] \tag{5}$$

and

$$pM' = \frac{1}{j+i}[pS - i \log (j/i)] - \frac{j}{j+i} \log \alpha_M - \frac{i}{j+i} \log \alpha_A \tag{6}$$

The pM' value, described as the masking coefficient of the salt M_jA_i is equal to the sum of three factors:

$-\frac{1}{j+i}[pS - i \log (j/i)]$ which describes the properties of the salt M_jA_i,

$-\frac{j}{j+i} \log \alpha_M$ which describes the effectiveness of cation masking,

and $-\frac{i}{j+i} \log \alpha_A$ which describes the effectiveness of anion masking.

The values of the first factor for various types of salts are summarised in Table I. On this basis it is possible to calculate it simply and rapidly for different salts; these data are given in Table II.

In the term depending on cation masking, α_M is equal to the ratio of total to free metal ion concentration and may be expressed as a function of stability constants of successive complexes:

$$\alpha_M = 1 + \beta_1[X] + \beta_2[X]^2 + \ldots \beta_n[X]^n \tag{7}$$

TABLE I—VALUES OF $\frac{1}{j+i}[pS - i\log(j/i)]$ FOR DIFFERENT SALT TYPES.

$j:i$	$\frac{1}{j+i}pS - [i\log(j/i)]$
1:4	$\frac{1}{5}pS + 0{\cdot}48$
1:3	$\frac{1}{4}pS + 0{\cdot}39$
2:5	$\frac{1}{7}pS + 0{\cdot}28$
1:2	$\frac{1}{3}pS + 0{\cdot}20$
2:3	$\frac{1}{5}pS + 0{\cdot}11$
3:4	$\frac{1}{7}pS + 0{\cdot}08$
1:1	$\frac{1}{2}pS$
4:3	$\frac{1}{7}pS - 0{\cdot}05$
3:2	$\frac{1}{5}pS - 0{\cdot}05$
2:1	$\frac{1}{3}pS - 0{\cdot}10$
5:2	$\frac{1}{7}pS - 0{\cdot}11$
3:1	$\frac{1}{4}pS - 0{\cdot}12$
4:1	$\frac{1}{5}pS - 0{\cdot}12$

TABLE II—VALUES OF $\frac{1}{j+i}[pS - i\log(j/i)]$ FOR VARIOUS SALTS.

Salt	Solubility product	$\frac{1}{j+i}[pS - \log(j/i)]$	Salt	Solubility product	$\frac{1}{j+1}[pS - \log(j/i)]$
AgOH	2×10^{-8}	3·85	$Cu(OH)_2$	$1{\cdot}6 \times 10^{-19}$	6·33
Ag_2CrO_4	$1{\cdot}3 \times 10^{-12}$	3·87	$Cu_2Fe(CN)_6$	$1{\cdot}3 \times 10^{-16}$	5·20
Ag_3PO_4	$1{\cdot}3 \times 10^{-20}$	4·85	$Cu(DDTC)_2$	$2{\cdot}8 \times 10^{-30}$	10·05
AgCl	$1{\cdot}8 \times 10^{-10}$	4·87	CuS	$8{\cdot}0 \times 10^{-36}$	17·55
$Ag_3Fe(CN)_6$	1×10^{-22}	5·38	$Cu_3(AsO_4)_2$	$7{\cdot}6 \times 10^{-36}$	6·97
AgNCS	1×10^{-12}	6·00	$Ni(OH)_2$	$2{\cdot}8 \times 10^{-16}$	5·38
AgBr	$4{\cdot}3 \times 10^{-13}$	6·13	$Ni(DDTC)_2$	$8{\cdot}5 \times 10^{-24}$	7·89
AgCN	$1{\cdot}2 \times 10^{-16}$	7·96	$Ni(DMG)_2$	2×10^{-22}	7·43
AgI	$8{\cdot}3 \times 10^{-17}$	8·04	NiS(α)	1×10^{-22}	11·0
$Ag_4Fe(CN)_6$	$1{\cdot}6 \times 10^{-41}$	8·04	$Zn(OH)_2$	$1{\cdot}9 \times 10^{-17}$	5·64
AgDDTC	$2{\cdot}6 \times 10^{-20}$	9·80	$Zn(DDTC)_2$	$1{\cdot}2 \times 10^{-17}$	5·84
Ag_2S	$5{\cdot}5 \times 10^{-51}$	16·65	ZnS	$1{\cdot}6 \times 10^{-22}$	11·4

DMG–dimethylglyoximate anion.
DDTC–diethyldithiocarbamate anion.
Values of solubility products at 25° are cited according to data listed in references 6 and 7 (for metal diethyldithiocarbamates).

where β_1, $\beta_2 \ldots \beta_n$ are successive overall stability constants, and $[X]$ is the concentration of the free masking ligand.

Calculation of α_M can easily be performed using a diagram which presents the relationship between the logarithm of α_M and the logarithm of free ligand concentration. Such diagrams have been cited in many papers dealing with conditional constants.[3,5] In Fig. 1 examples are given of ammonia, cyanide, EDTA and NTA (nitrilotriacetic acid) complexes of some metals.

In (7) the free ligand concentration, $[X]$, must be considered. If the analytical concentration of the ligand significantly exceeds the metal concentration, *i.e.* $C_A \gg C_M$, which usually happens in analytical masking reactions, and the ligand is the anion of a strong acid, or of a weak acid but at a given pH completely dissociated, the free ligand concentration is equal to its analytical concentration.

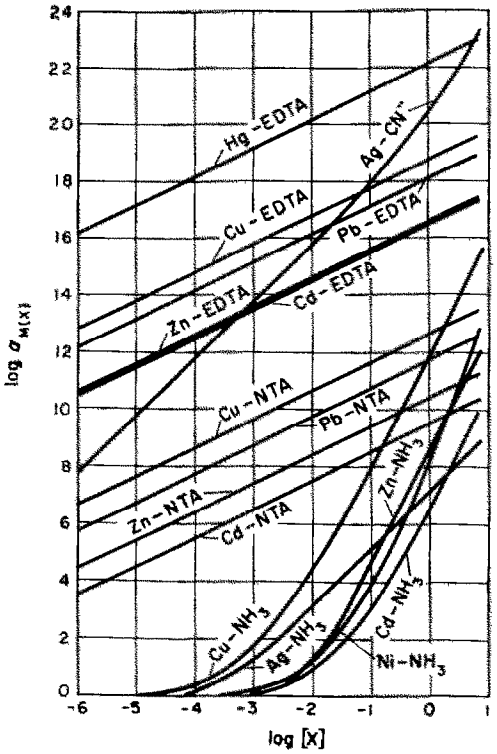


FIG. 1.—Diagrams of log $\alpha_{M(X)}$ *vs.* log [X] for some common metal complexes, plotted for $\mu = 0{\cdot}1$ and $t = 25°$ for NH_3-complexes,[8] NTA-complexes,[9] EDTA-complexes,[10] CN^--complex.[11] When appropriate data were not available approximate estimation was applied using data in slightly different conditions.

Otherwise the free ligand concentration should be calculated from known dissociation constants

$$[X] = \frac{C_X}{\alpha_{X(H)}} = \frac{C_X}{1 + k_1[H^+] + k_1k_2[H^+]^2 + \ldots} \tag{8}$$

or

$$\log [X] = \log C_X - \log \alpha_{X(H)} \tag{9}$$

where C_X represents the analytical concentration of the masking ligand, $\alpha_{X(H)}$ is the coefficient of side reaction for acid-base ligand dissociation and k_1, $k_2 \ldots$ are successive dissociation constants of the ligand.

The last term of (6) includes the effect of masking of salt anion. It is usually performed by pH changes, masking with hydrogen ion, but may also be realised by the presence of another metal ion, which forming stable complexes with the anion A decreases its effective concentration. The value of $\alpha_{A(H)}$ is given by:

$$\alpha_{A(H)} = 1 + k_1[H^+] + k_1k_2[H^+]^2 \ldots \tag{10}$$

but can be evaluated by means of appropriate diagrams. These diagrams are given in Fig. 2 for a number of anionic precipitants. The same figure can serve for calculation of $\alpha_{X(H)}$, the side reaction coefficient for acid-base dissociation of some complexing

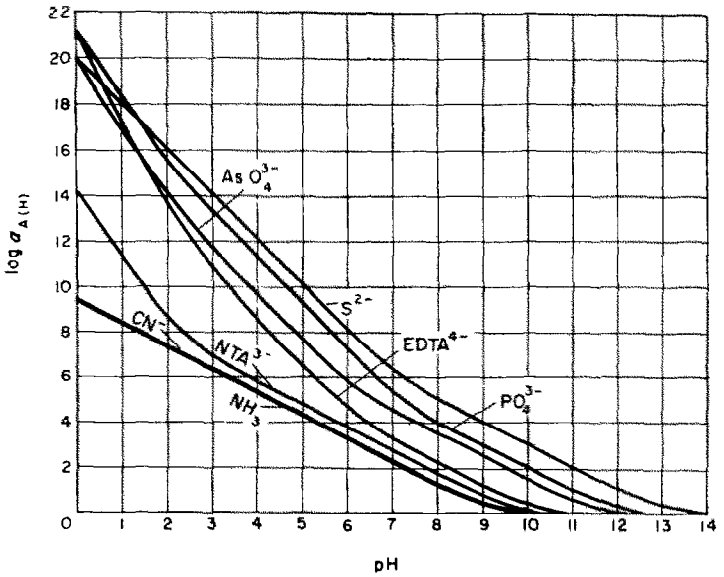


FIG. 2.—Diagrams of log $\alpha_{A(H)}$ or log $\alpha_{(XH)}$ *vs.* pH for some precipitating or complexing anions of weak acids, plotted for $\mu = 0{\cdot}1$ and t = 25°, for NH_3,[8] CN^-,[13] AsO_4^{3-},[13] PO_4^{3-},[14] S^{2-},[15] $EDTA^{4-}$,[16] NTA^{3-}.[9] When appropriate data were not available approximate estimation was applied using data in slightly different conditions.

agents used for masking. Thus obtained, log $\alpha_{X(H)}$, introduced in (9), makes possible evaluation of the logarithm of free ligand concentration.

Equation (6) makes possible the direct calculation of pM', *i.e.* the masking coefficient. The physical meaning of this magnitude is clearly seen from the derivation of (6). The resulting pM' value denotes simply the maximum analytical concentration of metal ion which can be present in given experimental conditions in equilibrium with an equivalent analytical concentration of the precipitate forming anion. Taking into account that in analytical procedures the metal concentration is usually of the order of $10^{-3} - 10^{-5}M$, complete masking can be expected if $pM' < 3$, and complete demasking if $pM' > 5$. Of course, for other conditions these limiting pM' values should be changed, respectively. An obvious significance of the pM' value enables a full understanding of the meaning of any obtained numerical pM' value. If its value is less than 3, or even negative, masking should be effective. The greater the pM' value, the more effective and complete the precipitation reaction and less disturbing the presence of a complexing agent.

EXAMPLES

To visualise more clearly the manner of calculation of pM' values and their practical application some examples are given below.

(a) For the masking of silver chloride ($pS = 9{\cdot}75$) by $0{\cdot}1M$ ammonia solution:

$$pM' = \tfrac{1}{2} \cdot 9{\cdot}8 - \tfrac{1}{2} \cdot 5{\cdot}0 = 2{\cdot}5.$$

The value of 2·5 indicates that no precipitation occurs in $0{\cdot}1M$ ammonia solution, unless the total silver concentration exceeds $10^{-2{\cdot}5}$ ($0{\cdot}003M$). In $1M$ ammonia

solution masking is more effective ($pM' = 1{\cdot}3$), and so in these conditions the silver concentration should not exceed $10^{-1{\cdot}3}$ ($0{\cdot}05M$).

(b) For the masking of silver ferricyanide ($pS = 22{\cdot}0$) by $0{\cdot}1M$ ammonia solution:

$$pM' = \tfrac{1}{4}[22{\cdot}0 - 0{\cdot}1] - \tfrac{3}{4} \cdot 5{\cdot}2 = 1{\cdot}6.$$

The value of 1·6 indicates that more effective masking occurs than in the previous example. This is in good agreement with experimental facts. In both cited examples the precipitating anion is completely dissociated in an ammoniacal medium and therefore the last term, containing α_A, in (6) can be omitted.

(c) Consider the precipitation of copper diethyldithiocarbamate ($pS = 29{\cdot}6$) in $0{\cdot}1M$ EDTA solution at pH 10. For $0{\cdot}1M$ EDTA solution at pH 10 the logarithm of the actual free ligand concentration, according to (9), is $-1{\cdot}0 - 0{\cdot}45 = -1{\cdot}45$. Therefore, from Fig. 1, for the copper-EDTA complex $\log \alpha_{Cu(EDTA)}$ is 17·4 and

$$pM' = \tfrac{1}{3}[29{\cdot}6 + 0{\cdot}6] - \tfrac{1}{3} \cdot 17{\cdot}4 = 4{\cdot}3.$$

In this example $\log \alpha_{DDTC}$ equals 0, because of complete dissociation of diethyldithiocarbamate at pH 10. The result indicates that, in spite of the precipitation of copper diethyldithiocarbamate, the masking is so strong that in a very dilute copper solution no precipitate can be formed, or the copper precipitation is not very complete. This is in good agreement with experiment.

(d) Consider the masking of copper arsenate ($pS = 35{\cdot}12$) by $0{\cdot}01M$ EDTA solution at pH 8·0. In this case both cation and anion are masked. The logarithm of actual free ligand ($EDTA^{-4}$) concentration is $-2{\cdot}0 - 4{\cdot}0 = -6{\cdot}0$, and $\log \alpha_{Cu(EDTA)}$ is 12·8, so that

$$pM' = \tfrac{1}{5}[35{\cdot}12 - 0{\cdot}25] - \tfrac{3}{5} \cdot 12{\cdot}8 - \tfrac{2}{5} \cdot 3{\cdot}5$$
$$= 7{\cdot}0 - 8{\cdot}1 - 1{\cdot}4 = -2{\cdot}5.$$

The negative value of pM' indicates very effective masking, which indeed takes place. Another conclusion from the calculation is that the decisive factor in this case is the masking of the cation, and masking of the arsenate by hydrogen ions plays a less important role.

(e) Consider the masking of silver phosphate ($pS = 19{\cdot}9$) by a hydrogen ion concentration of 10^{-3}. In this case only anion masking occurs, and therefore:

$$pM' = \tfrac{1}{4}[19{\cdot}9 - 0{\cdot}5] - \tfrac{1}{4} \cdot 14{\cdot}2 = 1{\cdot}30$$

which can be demonstrated experimentally.

DISCUSSION AND CONCLUSIONS

The introduction of a new term, the masking coefficient, has an important significance in the theoretical prediction of the direction in which a reaction will proceed in a complicated system containing a metal ion, a complexing and precipitating agent. The masking coefficient, pM', is expressed by the negative logarithm of the total metal concentration present in solution in equilibrium with the equivalent amount of a precipitant. The easily demonstrated physical significance of this expression makes possible its application in various analytical conditions. A border-value of pM' for either masking or precipitation of 3–5 is usual.

In a calculation of this type one must be warned not to expect a very high accuracy

of pM'. This follows from the limited accuracy of determination of various constants, *i.e.* solubility products, stability constants and dissociation constants. For these, especially in the determination of solubility products a rather significant error can be involved in most cases, which is connected with difficulties of attaining a true equilibrium between a solid phase and solution. Further, constants have been evaluated in various conditions of ionic strength, temperature and presence of foreign salts, and in most cases one is obliged to compare data not exactly corresponding to each other. All of these parameters influence the calculated masking coefficient and usually the reliability of the results is of the order of one, which corresponds to one order of concentration of the metal in solution.

The pM' value, taken with proper caution in accordance with the above mentioned facts, gives correct indications when the total metal concentration (not precipitated) and total precipitant concentration are equivalent. In practice this condition corresponds to a situation when one is going to dissolve a pure precipitate (not contaminated with any of the precipitate ions) in a masking agent. In some cases the equilibrium in such a system can be additionally shifted by adding an excess of precipitant. Theoretically, a sufficiently large excess can in any case cause precipitation, but practically the analyst is limited by conditions actually encountered. In the view of the present author, the properties of a system are most adequately described in the manner here proposed.

Acknowledgement—The author is greatly indebted to Professor Kemula for helpful and stimulating discussion concerning this work.

Zusammenfassung—Der "Maskierungskoeffizient" wurde als neuer Begriff abgeleitet und auf analytische Probleme im Zusammenhang mit der Maskierung von Fällungsreaktionen angewandt. Der Koeffizient is durch die folgende Gleichung definiert

$$pM' = \frac{1}{j+i}[pS - i\log(j/i)] - \frac{j}{j+i}\log\alpha_M - \frac{i}{j+i}\log\alpha_A$$

Das erste Glied bezieht sich auf Eigenschaften des Niederschlages, das zweite Glied auf die Maskierung des Kations und das dritte auf die Maskierung des Anions. Wenn geeignete Diagramme konstruiert wurden um die Seitenreaktionkoeffizienten $\log\alpha_M$ und $\log\alpha_A$ zu berechnen ist es leicht möglich alle Berechnungen durchzuführen. Die Vorraussagen (aufgrund der Berechnungen) ob Maskierung oder Fällung eintritt wurden experimentell geprüft und bestätigt. Einige Beispiele für Berechnungen analytisch gut bekannter Systeme werden gezeigt.

Résumé—Un nouveau terme, le "coefficient de dissimulation", a été introduit pratiquement dans les études analytiques mettant en jeu la formation de complexes dans les réactions de précipitation. Ce coefficient s'exprime par l'équation:

$$pM' = \frac{1}{j+i}\left[pS - i\log\left(\frac{j}{i}\right)\right] - \frac{j}{j+i}\log\alpha_M - \frac{i}{j+i}\log\alpha_A$$

dans laquelle le premier terme se rapporte seulement aux propriétés du précipité, le deuxième à la dissimulation du cation, le dernier à la dissimulation de l'anion. Si des diagrammes convenables ont été préparés pour le calcul des "coefficients de réaction secondaire", $\log\alpha_M$ et $\log\alpha_A$, tous les calculs peuvent etre effectués facilement. L'utilité du "coefficient de dissimulation", pour prévoir si la formation de complexes ou la précipitation va se produire, a été confirmée par l'expérience. Des exemples de calcul de ce coefficient, pour des réactions analytiques bien connues, sont donnés.

REFERENCES

[1] S. Chaberek and A. E. Martell, *Organic Sequestering Agents*. John Wiley & Sons, Inc., 1959.
[2] K. L. Cheng, *Analyt. Chem.*, 1961, **33**, 783.
[3] I. M. Kolthoff and P. J. Elving, *Treatise on Analytical Chemistry*. Interscience Publishers, 1959.
[4] R. Přibil, *Kompleksony w chimiczeskom Analizie*. Izd. Inostrannoj Literatury, 1960.

[5] A. Ringbom, *J. Chem. Educ.*, 1958, **35,** 282.
[6] A. F. Clifford, *Inorganic Chemistry of Qualitative Analysis.* Prentice-Hall. Inc., 1961.
[7] A. Hulanicki, *Acta Chim. Acad. Sci. Hung.*, 1961, **27,** 41.
[8] J. Bjerrum, *Metal ammine formation in aqueous solution.* Copenhagen, 1957.
[9] G. Schwarzenbach, G. Anderegg, W. Schneider and H. Senn, *Helv. Chim. Acta*, 1955, **38,** 1147.
[10] G. Schwarzenbach, R. Gut and G. Anderegg, *ibid.*, 1954, **37,** 937.
[11] M. Randall and J. O. Halford, *J. Amer. Chem. Soc.*, 1930, **52,** 178.
[12] H. T. S. Britton and E. N. Dodd, *J. Chem. Soc.*, 1931, 2332.
[13] A. L. Agafonowa and I. L. Agafonow, *Zhur. fiz. Khim.*, 1953, **27,** 1135.
[14] J. Beukenkamp, W. Rieman III and S. Lindenbaum, *Analyt. Chem.*, 1954, **26,** 505.
[15] J. R. Goates, M. B. Gordon and N. D. Faux, *J. Amer. Chem. Soc.*, 1952, **74,** 835.
[16] G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, 1947, **30,** 1798.

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DETERMINATION OF ^{90}STRONTIUM IN BONE*

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Summary—A procedure for the assay of ^{90}Sr in bone is presented, which is applicable for the determination of low levels of ^{90}Sr using ordinary counting equipment. The procedure involves extraction of the ^{90}Y daughter into a solution of dibutylphosphoric acid in scintillation fluid from a dilute nitric acid solution containing ^{90}Sr which had been concentrated from bone by the standard fuming nitric acid procedure. The extracted ^{90}Y in scintillation fluid can be counted directly without further preparation.

INTRODUCTION

NUMEROUS reports [1–5] on methods for the assay of ^{90}Sr in biological materials have been published over the past few years. Justification of adding still another to the literature lies in a novel approach to the problem, which simplifies ^{90}Sr assay in bone considerably, allows the use of ordinary counting equipment, and has potential application in the assay of other radioisotopes. The unique aspect of this procedure is extraction of the isotope to be assayed into a scintillation medium which can be counted without further preparation.[6]

In ^{90}Sr application, the procedure involves extraction of the ^{90}Y daughter by dibutylphosphoric acid in scintillation fluid from a dilute nitric acid solution containing ^{90}Sr which had been concentrated from bone by the standard fuming nitric acid procedure.[6] The basis for this procedure is an adaptation of a method for preparation of ^{90}Y by Dyrrsen.[7]

EXPERIMENTAL

Procedure

(1) To 100 g of bone ash powder add 50 ml of strontium carrier solution (10 mg of Sr^{2+}/ml in distilled water) and 30 ml of distilled water, followed by 225 ml of yellow fuming nitric acid (95%). Stir with a mechanical stirrer for 1 hr to ensure complete solution of the bone ash and precipitation of the strontium.

(2) Filter through a medium-grade sintered-glass suction filter, and discard the filtrate. Wash the precipitate with 80% nitric acid.

(3) Dissolve the precipitate by passing hot distilled water through the filter.

(4) Bring the solution of dissolved precipitate to a volume of approximately 50 ml and adjust to pH 1.

(5) Store the solution for 14 days for establishment of ^{90}Sr/^{90}Y equilibrium.

(6) Transfer the sample to a separatory funnel, and shake for 5 min with 40 ml of a mixture of 2·5% dibutylphosphoric acid, 0·05% POPOP,‡ and 0·5% *p*-terphenyl in toluene. Note the time of extraction. The dibutylphosphoric acid is purified by the method of Stewart and Crandall.[8]

(7) Separate the aqueous phase. This can be saved for repeated milking, if checks are necessary. Dry the organic portion with silica gel for approximately 15 min.

(8) Draw off 30 ml of organic phase into a 10-dram counting vial and count in a standard liquid scintillation counting set-up.[9] Note the counting time.

(9) Correct for decay of the ^{90}Y between time of extraction and time of counting.

(10) Recount the yttrium fraction at least twice more over a period of 1 week to determine the decay time of activity as a check on identity of the ^{90}Y.

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‡ 2,2′-*p*-Phenylenebis(5-phenyloxazole).

RESULTS AND DISCUSSION

The following studies and measurements were carried out to evaluate the procedure and to judge its merits.

Counting and extraction efficiency

Known amounts of ^{90}Sr were added to 0·1*N* nitric acid solution and extracted and counted by the method described above. This procedure was performed each day a "run" was done on a series of unknowns, to check reagents and counter. Results of 18 different determinations showed an average recovery of 90·58 ± 1·73%. When the nitric acid solution was re-extracted shortly after the first extraction, less than 1% of ^{90}Y was obtained, which indicated an essentially complete extraction in the first pass. The 10% or so diminution from the expected values undoubtedly was due to counting inefficiency.

*Recovery**

Each set of determinations included a blank consisting of tricalcium phosphate "spiked" with ^{90}Sr. This was run through as a check for over-all recovery in the procedure. The largest and most variable loss was found in the step involving separation of strontium and calcium by precipitation with fuming nitric acid. Final values were corrected by this recovery factor (see Table I).

TABLE I.—RECOVERY OF ^{90}STRONTIUM

^{90}Sr added, *d/min*	^{90}Sr recovered, *d/min*	Efficiency, %
35,774	32,898	91·96
39,384	35,032	88·95
76,799	67,506	87·90
41,025	33,673	82·08
13,128	9,900	75·41
16,410	11,983	73·02
147,149	119,529	80·90
97,147	79,048	81·37
	Average	82·70
	Standard deviation σ ±	6·70

Reproducibility

Table II shows the results for bone samples assayed in triplicate.

Sensitivity

To a large extent, interest in ^{90}Sr determinations lies in low-level samples. In our study, sample sizes of 100 g were used to gain sensitivity. However, smaller samples could have easily been used for good counting statistics without recourse to complicated counting with good equipment and prolonged counting times. Table III

* John Harley of the New York Operations Health and Safety Laboratory points out in a personal communication that a much more desirable recovery procedure can be accomplished by adding ^{85}Sr to each sample and then counting the strontium-separated solution in a scintillation γ-counter. In this way, each sample can be checked for recovery rather than each batch of samples, as was done in the procedure above.

shows the counting times necessary to obtain a given accuracy for samples at different levels of activity. Calculations are based on the following considerations:

(1) Fifty-g bone samples.
(2) Background equal to 70 c/min.
(3) Percentage standard deviation equals

$$\frac{100\sqrt{\frac{R_{(S+B)}}{t_{(S+B)}}+\frac{R_B}{t_B}}}{R_S} \quad \text{and} \quad \frac{t_{(S+B)}}{t_B}=\sqrt{\frac{R_{(S+B)}}{R_B}}$$

where $R_{(S+B)}$ = counting rate of sample plus background
R_B = counting rate of background
R_S = counting rate of sample
$t_{(S+B)}$ = time for counting sample plus background
t_B = time for counting background

TABLE II.—REPRODUCIBILITY OF RESULTS

Type of sample	Year	Place	^{90}Sr, *d/min/g*
Reindeer antler	1958	Alaska, USA	85·32; 86·38; 93·28
Elk antler	1956	Missouri, USA	23·25; 23·24; 22·17; 23·37; 23·46
Deer antler	1958	New Mexico, USA	12·61; 12·36; 12·06
Deer antler	1955	New Mexico, USA	5·35; 6·37; 6·80
Deer long bone	1957	New Mexico, USA	8·31; 9·80; 9·40; 10·08
Elk antler	1957	Colorado, USA	12·84; 12·13; 13·47
Elk skull	1957	Colorado, USA	17·07; 17·88; 18·13
Elk antler	1956	New Mexico, USA	8·47; 8·16; 8·45
Moose antler	1953	Yukon, Canada	2·21; 2·17; 2·30
Caribou antler	1953	Yukon, Canada	4·11; 5·35; 4·99

TABLE III.—COUNTING TIMES REQUIRED TO OBTAIN GIVEN ACCURACY

^{90}Sr content, *d/min/g*	Standard deviation, %	Counting time, *min*
5	10	< 1
	5	1·5
	1	35
1	10	6·4
	5	26
	2	160
0·5	10	24
	5	100
	2	608

As can be seen from the table, use of 50-g samples gives good counting statistics with reasonable counting times at the 1-d/min/g level of ^{90}Sr. At levels below this, it is advisable to use larger samples; at levels above this, smaller samples can be used advantageously.

Interfering isotopes

No specific attempt has been made to eliminate interfering radioisotopes in the procedure described above, since it was unnecessary in the studies judged by purity of ^{90}Y extracted. However, under certain conditions (*i.e.*, work with fresh fission product mixtures), it might be necessary to take steps to remove interfering activity. Both the strontium nitrate separation and the organic solvent extraction remove most interfering metals. However, lanthanum, lead, thorium, and radium daughters can appear in the final counting solution unless suitable measures are taken (*i.e.*, unless they are eliminated). ^{140}Lanthanum can be eliminated by removing ^{140}Ba through use of the chromate separation procedure described in the Harwell ^{90}Sr assay method. Lead and thorium are readily removed by a preliminary separation of the strontium solution with dibutylphosphoric acid/scintillator solution before the growth period of the yttrium. Radium daughters can be eliminated as interfering activity by boiling the strontium solution for 1 hr just before the final extraction of ^{90}Y.

Zusammenfassung—Eine Methode zur Bestimmung von geringen Mengen ^{90}Sr in Knochen unter Verwendung gewöhnlicher Zähleinrichtungen wird beschrieben. Das Tochterelement ^{90}Y wird in eine Lösung von Dibutylphosphorsäure in Scintillationflüssigkeit extrahiert und zwar aus der Lösung die das Strontium in verdünnter Salpetersäure enthält, wie es nach der üblichen Sappertsäureveraschung vorliegt. Das Yttrium wird ohne weitere Behandlung direkt gezählt.

Résumé—Les auteurs présentent une méthode de dosage de ^{90}Sr dans les os; cette méthode s'applique à détermination de faibles teneurs en ^{90}Sr permettant d'utiliser un équipement de comptage ordinaire. Le procédé met en jeu l'extraction de ^{90}Y formé par une solution d'acide dibutylphosphorique dans un fluide à scintillation à partir d'une solution d'acide nitrique diluée contenant ^{90}Sr; ce dernier a été concentré par la méthode courante de l'acide nitrique fumant. ^{90}Y extrait dans le fluide à scintillation peut être compté directement sans préparation ultérieure.

REFERENCES

[1] J. H. Harley and I. B. Whitney, *U.S. Atomic Energy Commission Report* NYOO-4700, 1957.
[2] E. A. Martell, *U.S. Atomic Energy Commission Report* AECU-3202, 1957.
[3] F. J. Bryant, A. Morgan and G. S. Spicer, *Atomic Energy Research Establishment Report* R-3030, 1959.
[4] H. L. Volchok, J. L. Kulp, W. R. Eckelmann and J. G. Gaetjen, *Ann. N.Y. Acad. Sci.*, 1957, **71**, 293.
[5] D. N. Sunderman and W. W. Meinke, *Analyt. Chem.*, 1957, **29**, 1578.
[6] H. H. Willard and E. W. Goodspeed, *Ind. Eng. Chem., Analyt.*, 1936, **8**, 414.
[7] D. Dyrrsen, *Acta Chem. Scand.*, 1957, **11**, 1277.
[8] D. C. Stewart and H. W. Crandall, *J. Amer. Chem. Soc.*, 1951, **73**, 1377.
[9] F. N. Hayes, *Internat. J. Appl. Radiation and Isotopes*, 1956, **1**, 45.

Talanta, 1962, Vol. 9, pp. 563 to 571. Pergamon Press Ltd. Printed in Northern Ireland

ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF SCANDIUM WITH TIRON

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Summary—A method is described for the spectrophotometric determination of 3–250 μg of scandium with tiron. The molar extinction coefficient of scandium in an acetate buffer (pH 6·0) is 8×10^3 at 310 mμ. Small amounts of aluminium, titanium, iron, cerium, molybdenum, thorium and zirconium seriously interfere. Organic anions such as oxalate, citrate, tartrate and malate form complexes with scandium. Both 1:1 and 1:3 complexes of scandium with tiron are suggested.

WELL established colour reagents are lacking for the spectrophotometric determination of scandium. Alizarin red S appears to be the reagent that has been utilised most successfully. A detailed separation procedure has been achieved for this reagent.[1] Scandium also gives a sensitive fluorescence reaction with morin[2] in neutral or weakly acidic solution. Recently, an oxine method[3] has been described, although it is highly unselective. A new photometric method for scandium using tiron is suggested in this paper.

Tiron (disodium 1,2-dihydroxybenzene-3,5-disulphonate) was first proposed by Yoe[4,5] as an analytical organic reagent for the determination of titanium and iron. The composition of their complexes has been determined by Harvey and Manning.[6,7] Schwarzenbach and Willi[8] have evaluated the stability constants of tiron-iron complexes by potentiometric and photometric methods. Photometric methods using tiron have also been described for the determination of traces of cerium,[9] niobium,[10] molybdenum[11,12] and uranium.[13]

Tiron reacts with scandium to give a colourless complex absorbing strongly at 310 mμ. The reaction is not selective, like other reagents for scandium, but it is very sensitive.

EXPERIMENTAL

Apparatus

A Hitachi Model EPU–2A spectrophotometer was used for making precise absorbance measurements at a given wavelength. Matched silica cells of 1·00-cm optical path were used. Measurements of pH were carried out with a Toa Dempa Model HM-5 pH-meter with glass and calomel electrodes. In the potentiometric titration of tiron in the absence of and in the presence of metal ions, measurements were made at 30° $\pm$ 0·05°.

Reagents

Standard scandium solution: 153·38 mg of scandium oxide (Yokosawa Chemical Co., Ltd.) were dissolved in 20 ml of concentrated hydrochloric acid and the solution was diluted to 100 ml with water. The strength of the stock solution was further checked by titration against ethylenedinitrilotetraacetate (EDTA) previously standardised against analytical reagent primary standard zinc metal, using Xylenol Orange[11,12] as indicator. This standard stock solution (1000 ppm of scandium) was diluted further as required.

0·10% *Tiron solution:* Prepared by dissolving 0·100 g of tiron (disodium 1,2-dihydroxybenzene-3,5-disulphonate) in 100 ml of water. The reagent stock solution was stable for at least 3 months.

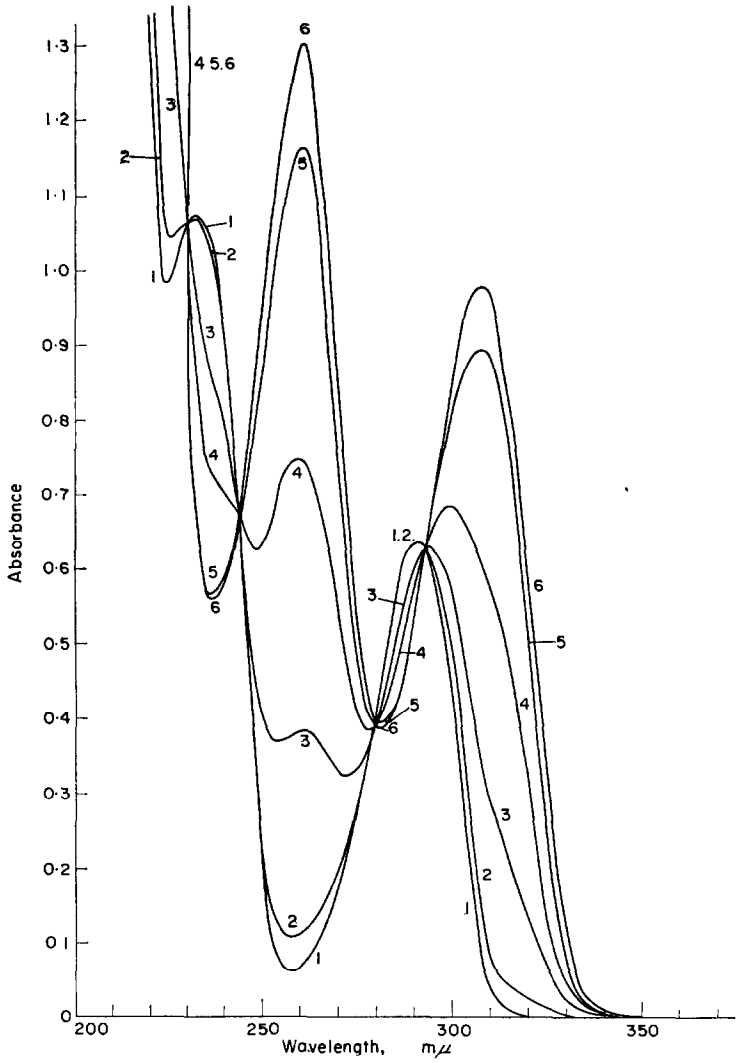


FIG. 1.—Absorption spectra for tiron at various pH values (concentration of tiron: $1{\cdot}86 \times 10^{-4}$ mole/litre):
(1) pH 5·90, (2) pH 6·80, (3) pH 7·77,
(4) pH 8·30, (5) pH 9·30 and (6) pH 10·80.

Solutions of diverse ions: The solutions of salts used in studying the effect of various ions were prepared to contain 1 mg/ml of the desired ion. All inorganic chemicals used were of reagent grade quality.

Acetate buffer solution (*pH* 6·0): Prepared by mixing 16 parts of 0·1*N* sodium acetate with 1 part of 0·1*N* acetic acid.

Ammonia-ammonium chloride buffer (*pH* 10·5): Prepared by mixing 32 parts of 0·1*N* ammonia solution with 1 part of 0·1*N* ammonium chloride.

Procedure:

Transfer the sample solution (dilute perchloric or hydrochloric acid solution) containing 3–250 μg of scandium to a 50-ml volumetric flask. Add 3 ml of 0·1% tiron solution and 20 ml of acetate buffer solution to adjust the pH to 6·0. If the acidity of the sample solution is too high, neutralise excess of acid with sodium hydroxide solution. After diluting to the mark with water and mixing, measure the absorbance of the solution in a 1-cm silica cell at 310 mμ against a reference solution containing the same amounts of tiron and the other reagents.

RESULTS AND DISCUSSION

Absorption spectra

To investigate the relation between pH and the absorption spectra, two series of solutions that contain tiron only and tiron plus scandium were prepared and scanned

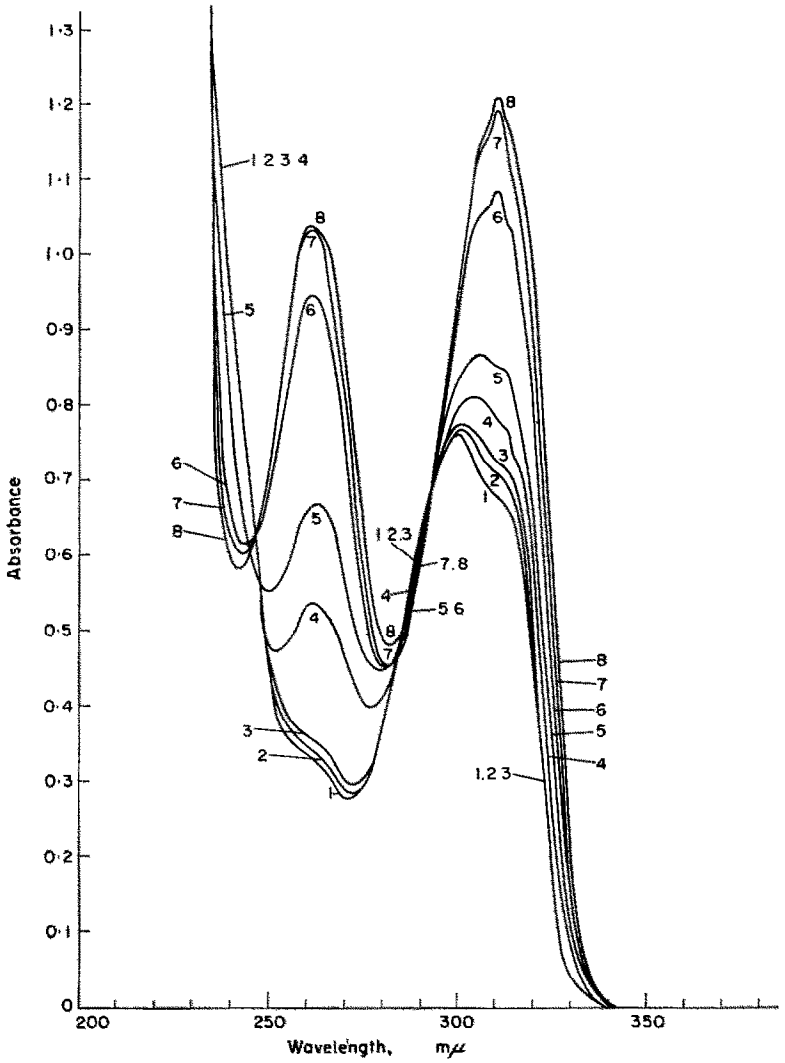


FIG. 2.—Absorption spectra for the scandium-tiron complex at various pH values (concentration of scandium: $7{\cdot}44 \times 10^{-8}$ mole/litre; concentration of tiron: $1{\cdot}86 \times 10^{-7}$ mole/litre):
(1) pH 3·61, (2) pH 5·92, (3) pH 6·46, (4) pH 7·58,
(5) pH 7·82, (6) pH 8·63, (7) pH 9·59 and (8) pH 11·30.

over the wavelength range from 220 to 350 mμ. The absorption spectrum of each solution was measured against water as a reference. The results are illustrated in Figs. 1 and 2. As shown in Fig. 1, the spectra of tiron exhibit pronounced absorption over the ultraviolet region with two peaks at 230 mμ and 290 mμ in the acidic media (<pH 6·80) and with two peaks at 260 mμ and 308 mμ in the alkaline ones. The complex

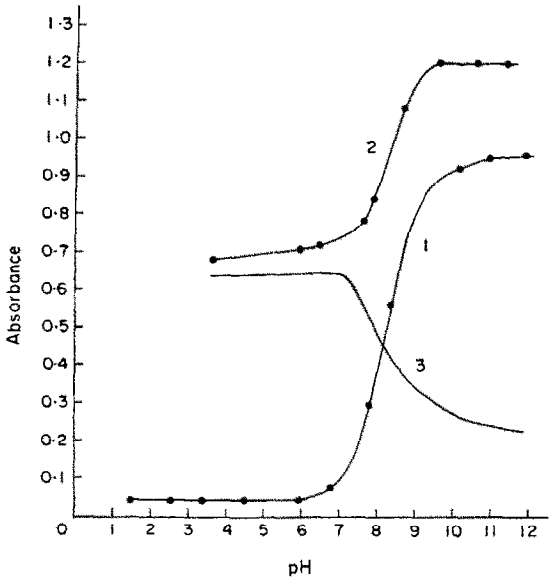


FIG. 3.—Effect of acidity on absorbance at 310 mμ.
(1) Tiron ($1{\cdot}86 \times 10^{-7}$ mole/litre) against water.
(2) Tiron ($1{\cdot}86 \times 10^{-7}$ mole/litre) plus scandium ($7{\cdot}44 \times 10^{-8}$ mole/litre) against water.
(3) Reagent blank.

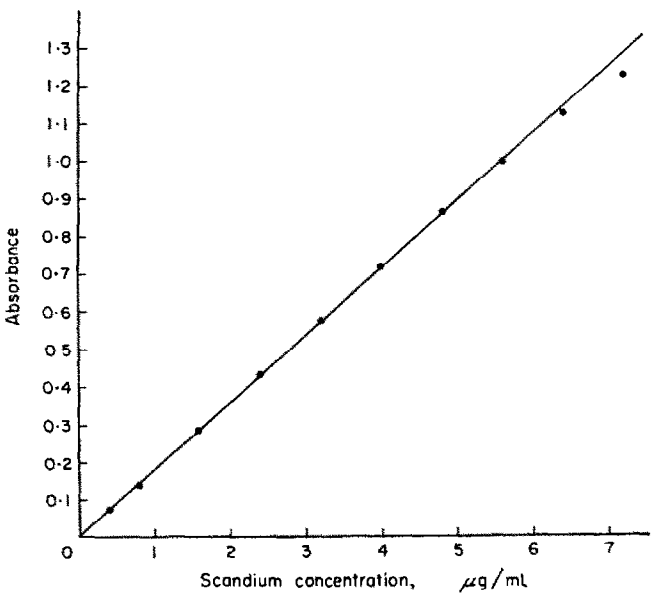


FIG. 4.—Scandium calibration curve.

also exhibits strong absorption in the ultraviolet region with a peak at 310 mμ over a wide range of pH values.

Effect of pH

pH has a considerable effect on the absorption of the complex at 310 mμ, as illustrated in Fig. 3. Curve 1 indicates the effect of pH on the absorbance of tiron measured

against water at 310 mμ and curve 2 the effect on that of the complex. Subtracting curve 2 from 1, curve 3 results, which is the net absorbance of the complex. At pH values ranging from 7 to 3·5, the absorbance of the complex is almost constant.

Effect of tiron concentration

A study of the variation in the net absorbance (310 mμ) of the complex at pH 6·0 as a function of the amount of tiron added indicated that reaction is complete when at least 3 times as much tiron as the amount of scandium is present.

Time of standing

The scandium-tiron complex forms almost instantly at pH 6·0 and an essentially constant absorbance reading is obtained over a period of at least 2 hr.

Conformity to Beer's law

The linearity between the absorbance of the scandium-tiron complex and the scandium concentration was tested by varying the scandium concentration in a number of test solutions and measuring the absorbances at a wavelength of 310 mμ and pH 6·0. As shown in Fig. 4, the absorbance is proportional to the scandium concentration in the range of 0·05 to at least 5 ppm of scandium (3–250 μg per 50 ml). At 310 mμ the molar extinction coefficient is 8×10^3. The spectrophotometric sensitivity is estimated to be 0·05 μg of scandium/cm^3, corresponding to $\log I_0/I = 0{\cdot}001$.

Composition of the scandium-tiron complexes

The composition of the scandium-tiron complexes was determined by Job's method of continuous variation. The experiments were carried out at room temperatures ranging from 25 to 29°. Two series of eleven solutions were prepared, each containing scandium and tiron in different proportions, but in each solution the combined concentration of scandium and tiron was always $9{\cdot}03 \times 10^{-6}$ mole per 50 ml. These two series of solutions were adjusted to pH 6·0 and 10·5 by adding the acetate and ammonia buffer solutions, respectively. Ten ml of 0·1*N* sodium acetate solution were added to each solution (pH 8·5, 10·5, 12·7) to prevent hydrolysis of scandium.

The results confirm the presence of two types of complex according to the pH range. Throughout the survey by Job's method over the possible pH range it is indicated that 1:1 and 3:1 complexes in ligand: metal ratio can exist below pH 6·5 and above 8·5, respectively. Typical Job's continuous variation plots at pH 6·0 and 10·5 are illustrated in Figs. 5 and 6, respectively.

Potentiometric titration curves of solutions containing 1 and 3 moles of ligand per mole of scandium offer additional information about the nature of the chelating process.

The curves for the system are shown in Fig. 7, in which the abscissa denotes the number of moles of standard base added per mole of scandium ion (n). It is found from curve 1 that the reaction of scandium^{III} ions with tiron results in the liberation of 1 mole of hydrogen ion per mole of scandium ion before the first pronounced inflection occurs at n = 1. The first reaction step corresponds to the formation of the 1:1 metal chelate in accordance with the reaction:

$$(HO)_2L^{2-} + Sc(H_2O)_6^{3+} + OH^- \rightarrow ScO(OH)L{\cdot}(H_2O)_5 + 2H_2O$$

where $(HO)_2L^{2-}$ denotes tiron in solution. Further reaction with a second mole of hydroxyl ion is indicated by the fact that the titration curve has an additional buffer region and a second inflection at 2 moles of base per mole of scandium ion.

This reaction cannot be explained as being associated with the formation of a higher

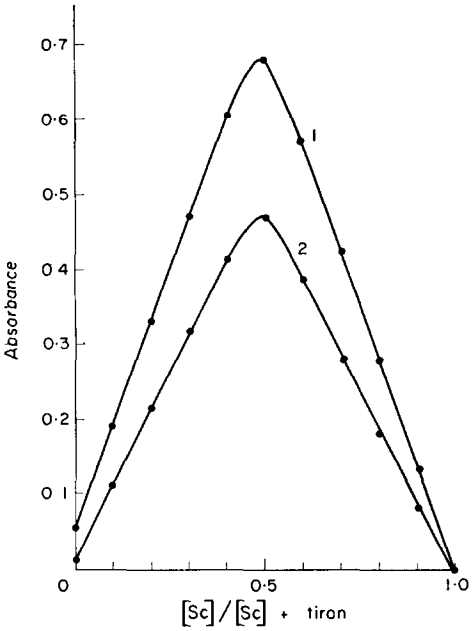


FIG. 5.—Continuous variation plot for the scandium-tiron complex at pH 6·00: (1) 310 mμ, and (2) 320 mμ.

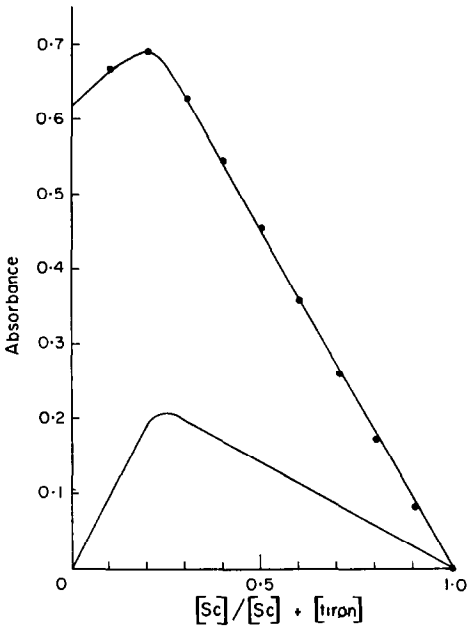
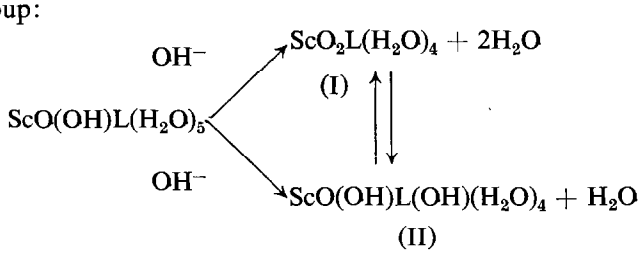


FIG. 6.—Continuous variation plot for the scandium-tiron complex at pH 10·48.

chelate. If the formation of a higher chelate results, the following disproportionation reaction should be postulated:

$$ScO(OH)L + OH^- \rightarrow \tfrac{1}{3}Sc_2[O(OH)L]_3 + \tfrac{1}{3}Sc(OH)_3.$$

No precipitation occurs throughout the titration range. Therefore, the possibility of the formation of a 2:3 chelate can be eliminated. As a result possible reaction at $n = 2$ appears to be such that the second reaction step involves the neutralisation of a hydrogen ion from either the co-ordinated water molecule or the co-ordinated phenolic hydroxy group:



Structure I involves the species resulting from neutralisation of a hydrogen from the co-ordinated phenolic hydroxy group and structure II corresponds to a hydroxo complex species resulting from neutralisation of a hydrogen from the co-ordinated

water molecule. Structures I and II are tautomeric and the metal chelate in solution may actually be an equilibrium mixture of the two forms.

Titration curve 2 of the solution containing a 1:3 mole ratio of scandium and tiron also has an inflection point at n = 1, in accordance with the formation of a 1:1

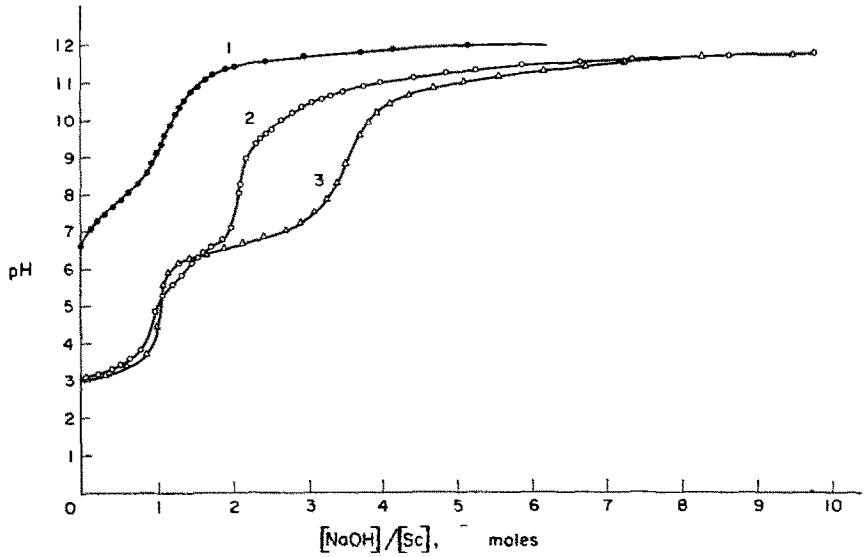


FIG. 7.—Titration curves of tiron and tiron-scandium complexes in 0·1*N* potassium chloride solution:
(1) Tiron = 10^{-3} mole/litre.
(2) Tiron: Scandium = $3{\cdot}71 \times 10^{-4}$ mole/litre.
(3) Tiron = $1{\cdot}11 \times 10^{-3}$ mole/litre and scandium = $3{\cdot}71 \times 10^{-4}$ mole/litre.

chelate in solution. A rather obscure second inflection point is observed at n = 3. The second reaction step of the 1:3 titration may be represented by:

$$ScO(OH)L(H_2O)_5 + 2(HO)_2L + 2OH^- \rightarrow Sc[O(OH)L]_3(H_2O)_3 + 4H_2O.$$

The formation of a monohydroxo complex can occur, however, above pH 7, as indicated in the titration of the solution containing a 1:1 metal:ligand ratio. The possibility could not be overlooked of the formation of higher hydroxo complexes including two or three hydroxyl groups in the pH range above 9. Competitive formation of these complexes against that of $Sc[O(OH)L]_3(H_2O)_3$ may be thought of as a possible cause for the rather obscure occurrence of the second inflection points in the titration of the 1:3 mixture.

Effect of diverse ions

The effect of many ions on the determination of scandium was studied under the conditions used in the proposed procedure. The results are summarised in Table I.

Table I suggests that the common cations known to react with tiron seriously interfere. The anions in Table I also diminish the absorbancy of solutions. Chloride, perchlorate, and nitrate do not interfere.

To overcome difficulties from interfering ions the following procedure for separating scandium by a cation exchanger seems to be valuable.

TABLE I.—EFFECT OF DIVERSE IONS

Interfering ions	Ions added, $\mu g/ml$	Sc found,[a] $\mu g/ml$	Ions added, $\mu g/ml$	Sc found,[b] $\mu g/ml$
Al^{3+} (as nitrate)	3	6·50	30	∞
Sn^{4+} (as sulfate)	3	3·82	30	0·00[c]
Fe^{3+} (as chloride)	3	6·72	30	∞
Fe^{2+} (as chloride, ascorbic acid added)	3	6·42	30	5·79
Ce^{4+} (as nitrate)	3	4·34	30	6·95
La^{3+} (as oxide)	3	4·15	30	2·04
Mo^{6+} (as ammonium molybdate)	3	4·11	30	6·51
Th^{4+} (as nitrate)	3	4·73	30	7·00
Zr^{4+} (as oxychloride)	3	4·63	30	∞
Oxalate	3	3·48	30	0·20
Citrate	3	3·12	30	0·00
Tartrate	3	3·08	30	0·74
Malate	3	2·84	30	0·42
NH_4SCN	3	3·88	30	1·22

[a] 4·05 μg/ml of Sc taken.
[b] 1·35 μg/ml of Sc taken.
[c] Because the 1:6 titanium-tiron complex is suggested by Yoe, free reagents in the test solution may not exist.

Prepare a column, 20 cm in length and 1·1 cm in diameter and packed at the bottom with glass wool. Slurry 10 g of the cation-exchange resin (Diaion SK 1, styrene-base strong acid type, equivalent to Dowex 50–x8, 100–200 mesh, hydrogen form) into the column. The height of resin bed usually amounts to approximately 16 cm. Before use the column is conditioned by running a solution, 2*M* in ammonium thiocyanate and 1*M* in hydrochloric acid, then converted to the hydrogen form with 3*M* hydrochloric acid and washed with water. Load the sample solution containing 1–2 mg of scandium onto the column. Rinse the column with small amounts of water. For separating scandium from rare earths and thorium elute with a solution 1*M* in ammonium thiocyanate and 0·5*M* in hydrochloric acid, collecting the effluent containing scandium. Rare earths and thorium remain on the column. If necessary, they are detached from the column by elution with a solution 2*M* in ammonium thiocyanate and 0·5*M* in hydrochloric acid. Iron and aluminium can be readily eluted by the same elutriant as for scandium prior to leakage of scandium. Iron may effectively be eluted even with more dilute elutriant, say 0·5*M* in ammonium thiocyanate and 0·5*M* in hydrochloric acid. Scandium is then detached with 3*M* hydrochloric acid or, more easily, with the solution 2*M* in ammonium thiocyanate and 0·5*M* in hydrochloric acid. The separation of titanium and zirconium is also possible. Titanium is completely separated from scandium by eluting it with the elutriant 0·5*M* in ammonium thiocyanate and 0·5*M* in hydrochloric acid, leaving scandium remaining on the column. To separate zirconium the use of an

TABLE II.—SEPARATION OF SCANDIUM FROM INTERFERING IONS

Interfering ion	Ion added, *mg*	Sc added, *mg*	Sc found, *mg*
Al^{3+}	5·60	2·37	2·43
Ti^{4+}	1·50	2·27	2·29
Fe^{3+}	14·14	2·40	2·24
La^{3+}	15·12	2·27	2·42
Sm^{3+}	4·73	2·27	2·27
Th^{4+}	4·76	2·37	2·37
La^{3+} + Th^{4+}	15·12 + 8·52	2·27	2·27
Zr^{4+}	2·70	2·27	2·21

elutriant 1*M* in ammonium thiocyanate and 1*M* in hydrochloric acid is recommended. Zirconium is eluted prior to scandium. To assure complete separation of zirconium, however, a somewhat longer column than that suggested above is desirable.

After destroying the ammonium thiocyanate with nitric acid and fuming with perchloric acid, scandium can be successfully determined photometrically with tiron. Scandium is also conveniently determined by an EDTA titration method in the presence of thiocyanate using Xylenol Orange as indicator at pH 3·5. Table II lists some results on the separation of scandium from interfering ions given in Table I. Scandium was determined by the EDTA titration method in the presence of ammonium thiocyanate. A detailed account of the ion-exchange separation of scandium will be published later.

Zusammenfassung—Eine Methode zur Bestimmung von 3–250 μg Scandium mit Tiron wird beschrieben. Der molare Absorptionskoeffizient des Scandiumkomplexes in Acetatpuffer von pH 6 beträgt 8000 bei 310 mμ. Bereits kleine Mengen von Al, Ti, Fe, Ce, Mo, Th und Zr stören beträchtlich. Oxalat-, Citrat-, Tartrat- und Malation stören durch Komplexierung des Scandiums. Evidenz für 1:1 und 1:3 Komplexe zwischen Scandium und Tiron wird nachgewiesen.

Résumé—Les auteurs décrivent une méthode de dosage spectrophotométrique de 3 à 250 μg de scandium par le tiron. Le coefficient d'extinction molaire du scandium en tampon acétate (pH 6,0) est de $8 . 10^3$ à 310 mμ. De faibles quantités d'aluminium, de titane, de fer, de cérium, de molybdène, de thorium et de zirconium gênent sérieusement. Les anions organiques comme les acides oxalique, citrique, tartrique et malique forment des complexes avec le scandium. Les auteurs suggèrent la formation des complexes scandium-tiron 1/1 et 1/3.

REFERENCES

[1] A. R. Eberle and M. W. Lerner, *Analyt. Chem.*, 1955, **27**, 1551.
[2] E. B. Sandell, *Colorimetric Determination of Traces of Metals*. Interscience Publishers, Inc., New York, 1959. p. 800.
[3] F. Umland and H. Puchelt, *Analyt. Chim. Acta*, 1957, **16**, 334.
[4] J. H. Yoe and A. R. Armstrong, *Ind. Eng. Chem., Analyt.*, 1947, **19**, 100.
[5] J. H. Yoe and A. L. Jones, *ibid.*, 1944, **16**, 111.
[6] A. E. Harvey and D. L. Manning, *J. Amer. Chem. Soc.*, 1950, **72**, 4488.
[7] *Idem, ibid.*, 1952, **74**, 4744.
[8] G. Schwarzenbach and A. Willi, *Helv. Chim. Acta*, 1951, **34**, 528.
[9] B. Sarma, *J. Sci. Ind. Res., India*, 1956, **15B**, 696; *Chem. Abs.*, 1957, **51**, 17572.
[10] H. Flaschka and E. Lassner, *Michrochim. Acta*, 1956, 778.
[11] B. Sarma *J. Sci. Ind. Res., India*, 1957, **16B**, 478; *Chem. Abs.*, 1958, **52**, 5203.
[12] F. Willi III and J. H. Yoe, *Analyt. Chim. Acta*, 1953, **8**, 546.
[13] B. Sarma and C. P. Savariar, *J. Sci. Ind. Res., India*, 1957, **16B**, 80; *Chem. Abs.*, 1957, **51**, 11168
[14] J. Körbl and R. Přibil, *Chem. Analyst*, 1956, **45**, 102.
[15] J. Körbl, R. Přibil and A. Emr, *Chem. Listy*, 1956, **50**, 1440; *Coll. Chem. Czech. Comm.*, 1957, **22**, 961.

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SALTING-OUT CHROMATOGRAPHY—VIII§

ANALYSIS OF MIXTURES OF MONOALKYL ESTERS OF ALKANE-PHOSPHONIC ACIDS AND DIALKYL ESTERS OF PHOSPHORIC ACID

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Summary—A method is described for the determination of each compound in a mixture of 19 acids of phosphorus.

THIS investigation was concerned with the analysis of mixtures of the phosphorus-containing decomposition products of certain insecticides and related compounds. The compounds studied were orthophosphoric acid, methanephosphonic acid, the dialkyl esters of orthophosphoric acid and the monoalkyl esters of the alkanephosphonic acids, The alkyl groups found in these compounds were methyl, ethyl, isopropyl and n-butyl, hereinafter designated as Me, Et, Pr, and Bu, respectively.

The marked similarity of chemical and physical properties of these compounds made it unlikely that quantitative separation of them could be achieved by paper chromatography. Attempts to use gas chromatography[1] were unsuccessful because the compounds were insufficiently volatile. Anion-exchange chromatography also failed to yield quantitative separations[1] because of the very small differences in the ionisation constants of the acids and in the selectivity coefficients of their conjugate bases.[1–3] As reported previously[4] for the analysis of a simpler mixture of organophosphorus acids, salting-out chromatography with low-capacity Dowex cation-exchange resins was found to be more successful than anion-exchange chromatography.

DEVELOPMENT OF THE METHOD

Preliminary elutions through the previously described low-capacity cation exchangers[4] indicated that the elution graphs were essentially Gaussian if the column was maintained at 50° and the flow rate at about 0·15 cm per min. These conditions were used throughout the work.

Evaluation of C *and* P

Each phosphorus compound was eluted individually several times, each time with a different concentration of LiCl and/or HCl. From the resulting elution graphs, the values of C and P were calculated for each compound with each eluent. C denotes the distribution ratio, and P the number of plates per cm of column. The equations for calculating these parameters from an elution graph are given elsewhere.[5,6] The values of P depended on the compound being eluted and on the eluent. The average P was 20. The values of C are given in Table I.

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§ Part VII—see reference 4.

Major elution

From these values, the minimum length of column required for a quantitative separation of all 19 compounds in one elution was calculated.[5,6] The calculations revealed that the quantitative separation of compounds 5 and 6 (Table I) with 4*M* LiCl + 1*M* HCl (P = 20) requires a column 5,100 cm long. This figure demonstrates

TABLE I.—VALUES OF LOG C OF THE PHOSPHORUS ACIDS

No.	Compound	Group	No LiCl 1*M* HCl	2 *M* LiCl 1 *M* HCl	4 *M* LiCl 1 *M* HCl	6 *M* LiCl 1 *M* HCl	8 *M* LiCl 1 *M* HCl
1	H_3PO_4				−0·018		+0·056
2	$MePO(OH)_2$				+0·216	0·301	0·417
3	MePO(OH)OMe	1		0·425	0·479	0·583	0·700
4	$HOPO(OMe)_2$	1		0·400	0·476	0·648	0·927
5	MePO(OH)OEt	2		0·550	0·715	0·811	0·997
6	EtPO(OH)OMe	2		0·553	0·694	0·823	1·045
7	MePO(OH)OPr	3		0·673	0·870	1·033	1·299
8	EtPO(OH)OEt	3		0·725	0·892	1·093	1·387
9	$HOPO(OEt)_2$	3	0·505	0·741	0·934	1·196	
10	EtPO(OH)OPr	4	0·690	0·865	1·045	1·314	
11	PrPO(OH)OEt	4	0·740	0·899	1·107	1·346	
12	MePO(OH)OBu	5	0·789	1·029	1·250	1·525	
13	$HOPO(OPr)_2$	5	0·763	1·045	1·309	1·643	
14	BuPO(OH)OMe	5	0·832	1·049	1·281	1·551	
15	BuPO(OH)OEt	6	0·991	1·236	1·509	1·823	
16	EtPO(OH)OBu	6	1·000	1·250	1·516	1·841	
17	PrPO(OH)OBu		1·186	1·477			
18	$HOPO(OBu)_2$		1·405	1·812			
19	BuPO(OH)OBu		1·467	1·820			

the impracticability of separating all 19 compounds in a single elution. Further calculations revealed that a column 50 cm in length should isolate compounds 1, 2, 17, 18 and 19 from all the others and also separate the others into six groups of "inseparable compounds" as indicated in Table I. It was therefore decided to use a 50-cm column for the "major elution" and to devise other methods for the determination of the individual compounds in each of the six groups.

It was very desirable to change the concentration of LiCl in the eluent during the major elution. If dilute LiCl were used exclusively, the more hydrophilic compounds of phosphorus would be eluted very rapidly and appear very incompletely separated in the first few hundred ml of eluate. On the other hand, if concentrated LiCl were used exclusively, very large volumes of eluent, and hence long periods of time, would be required to elute the more hydrophobic compounds. For example, with 4*M* LiCl + 1*M* HCl as eluent and with a column of the dimensions finally selected, 50·5 cm × 2·51 cm^2, the peak of compound 16 would appear at 2,220 ml. Although the C values of compounds 17, 18 and 19 were not determined with this eluent it is certain that more than 3 litres would be required to complete the elution.

Several preliminary experiments indicated that the sequence of eluents given in Fig. 1 was most satisfactory. Perhaps a gradient change in eluent concentration would be more efficient but the stepwise changes were preferred because it would have been much more difficult to devise a satisfactory gradient.

Fig. 1 shows the results of two elutions. The continuous line represents the elution of a mixture of compounds 1, 2, 3, 5, 9, 10, 13, 15, 17, 18 and 19. The dotted line

represents the elution of a mixture of compounds 4, 6, 7, 8, 11, 12, 15 and 16. Compound 14 was inadvertently omitted from the second mixture, but other experiments demonstrated that it is quantitatively contained in the eluate fraction from 575 to 700 ml. Fig. 1 confirms the calculations, mentioned above, that a 50-cm column should separate the mixture of all 19 phosphorus compounds into five compounds and six groups.

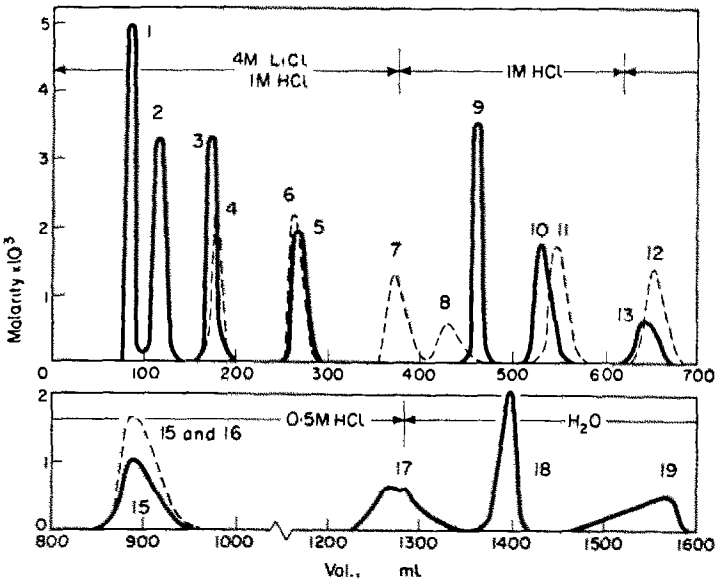


FIG. 1.—Chromatogram of the "major elution"
Column 50·5 cm × 2·51 cm², Temp. 50° ± 1°, Flow rate 0·05 to 0·15 cm/min. Sequence of eluents: 4*M* LiCl + 1*M* HCl-0 to 374 ml, 1*M* HCl-374 to 614 ml, 0·5*M* HCl-614 to 1264 ml, H_2O-1264 to 1600 ml.

Hydrolysis of the esters

It remained to devise methods of determining each compound in the "inseparable groups."

Inspection of Table I revealed that the chief factor governing the C values with any given eluent is the number of carbon atoms per molecule and that structural considerations are relatively unimportant. Further inspection of Table I revealed that the hydrolytic removal of the alkoxyl groups from the compounds in any group will yield phosphorus compounds differing from each other in their carbon content. For example, hydrolysis of Group 2 should yield $MePO(OH)_2$ and $EtPO(OH)_2$. These compounds should be readily separable by a secondary elution. Preliminary experiments[3] proved that the alkoxyl groups are quantitatively removed from all of the compounds by refluxing for 2·5 hr with 6*M* HCl.

Separation of the phosphorus compounds from HCl *and/or* LiCl

Still another preliminary step was necessary before the secondary elutions could be successful. Groups 4, 5 and 6 were found in the eluate along with large amounts of HCl. Groups 1, 2 and 3 were found in the eluate accompanied by large quantities of both HCl and LiCl. Each group of phosphorus compounds had to be separated from

almost all of these electrolytes in order that it could be dissolved in a small volume and applied to the column for the secondary elution.

The removal of HCl from Groups 4, 5 and 6 presented no difficulty. It was accomplished simply by evaporation in a vacuum to a small volume.

For the analysis of Group 1, a non-chromatographic method was devised that did not require the removal of LiCl or HCl.

For the analysis of Groups 2 and 3, however, the removal of these electrolytes was essential and presented considerable difficulty. Among the inefficient or unsuccessful methods investigated were liquid-liquid extraction with chloroform, solid-liquid extraction after evaporation to dryness, precipitation of the organophosphorus anion, gathering by aluminium hydroxide and ion exclusion. Finally, at the suggestion of Dr. Yurow,[7] selective adsorption of the phosphorus compounds by cellulose impregnated with zirconia was tried. This method proved to be successful. By passage of an acid solution of the mixture through a column of the impregnated cellulose, the phosphorus compounds were retained on the column while the LiCl passed through. The phosphorus compounds were then recovered by passing dilute ammonia through the column.

DETAILS OF THE PROCEDURE

Reagents

Most of the phosphorus compounds were supplied by the Army Chemical Center. The low-capacity cation-exchange resin has been described previously.[4] It was used in columns provided with water jackets through which water at 50° ± 1° was pumped. A Rinco Rotating Vacuum-type Evaporator, Model VE-1000-A, was used to evaporate solutions without application of heat.

The cellulose impregnated with zirconia was prepared as follows: Ten g of cellulose powder were mixed with a hot solution of 10 g of zirconyl nitrate in 100 ml of 1*M* sulphuric acid. After filtration with suction, the cellulose was dried on a glass plate at room temperature for 48 hr. It was then passed through a 40-mesh sieve and slowly added with stirring to 100 ml of 3*M* ammonia. It was filtered again and washed with three 100-ml portions of water. It was stored in 0·01*M* hydrochloric acid. A column of 0·76 cm^2 cross-sectional area was filled to a depth of 12·5 cm with this material.

Samples of the mixture of phosphorus compounds were prepared for analysis by pipetting a known volume of a standard solution of each compound into a beaker and evaporating the solution to dryness in a vacuum oven at room temperature. A known volume of the first eluent, 4*M* LiCl + 1*M* HCl, was added to dissolve the residue.

Major elution

An aliquot of 2·00 ml of the foregoing solution was pipetted carefully into the chromatographic tube. The solution was drained to the top of the resin bed. Three portions of 2 ml of the first eluent were added; each portion was applied so as to rinse the inside walls of the tube and was drained to the level of the resin before the next was added. The collection of 5·5-ml fractions of eluate was started with the addition of the sample. In changing eluents, each eluent was drained to the level of the resin before the next was added. Care was taken not to permit air to enter the column. The fractions of eluate containing any one isolated compound of phosphorus or any one inseparable group were combined, as indicated by Fig. 1.

With each change of eluent, the resin expanded. The first effect of this swelling was a decrease in the interstitial volume, and hence a decrease in flow rate to about 0·05 cm per min with the same hydrostatic head. However, the column length gradually expanded, thus increasing the flow rate to about the original value of 0·15 cm per min. The final length of column was 88 cm.

Analysis of eluate fractions

A suitable aliquot of the eluate fraction containing compound 1, 2, 17, 18 or 19 was analysed by converting the organophosphorus compound to orthophosphate by treatment with alkaline persulphate and subsequent spectrophotometric determination of the orthophosphate. Details of this procedure have been published elsewhere.[4,8]

Group 1 contains MePO(OH)OMe and $HOPO(OMe)_2$ mixed with LiCl and HCl. An aliquot containing not more than 40 meq of LiCl was mixed with an equal volume of 12*M* HCl and refluxed for 2·5 hr to convert the phosphorus compounds to $MePO(OH)_2$ and H_3PO_4, respectively. The solution was evaporated to dryness to get rid of the acid. The residue was dissolved in water and diluted to

100 ml in a volumetric flask. An aliquot of this solution was treated with alkaline persulphate to convert the methanephosphonate to orthophosphate. Details of this step have been published elsewhere.[4,8] Then the total phosphorus in this solution was determined by the spectrophotometric method of Barton.[9]

Another aliquot of the solution was treated by the method of Barton without the application of persulphate. Thus only orthophosphate was determined because $MePO(OH)_2$ does not give a colour reaction with vanadomolybdate reagent. From the results of these two determinations, the quantity of each organophosphorus compound in the group was calculated.

Group 2 contains MePO(OH)OEt and EtPO(OH)OMe mixed with LiCl and HCl. The pH was adjusted to 2·0 with NaOH and HCl. The solution was then passed through the column of cellulose impregnated with zirconia at 2·7 ml per min. Then 100 ml of 0·01*M* HCl was passed through the column. Thus all the lithium was found in the effluent and all the organophosphorus compounds in the column. Elution with 100 ml of 0·1*M* ammonia served to elute the latter completely. This solution was evaporated to about 10 ml, mixed with an equal volume of 12*M* HCl and refluxed for 2·5 hr to convert the phosphorus compounds to $MePO(OH)_2$ and $EtPO(OH)_2$, respectively. This solution was evaporated to dryness under vacuum to remove the HCl. The residue was dissolved in a measured volume of 8*M* LiCl + 1*M* HCl. An aliquot of this solution was transferred to a column, 12·5 cm × 3·82 cm², of the low-capacity cation exchanger and eluted at 50° with 8*M* LiCl + 1*M* HCl. The elution

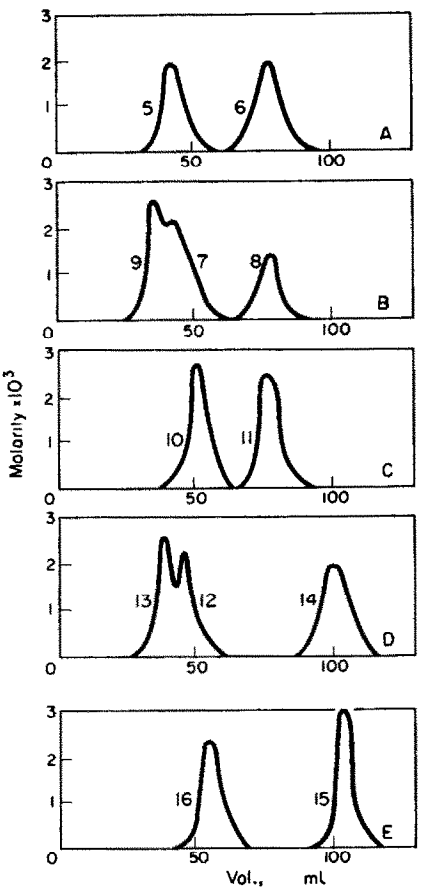


FIG. 2.—Chromatogram of the "secondary elutions"

Temp. 50° ± 1° Flow rate approx. 0·15 cm/min.
A and B: Column 19 cm × 3·8 cm²; eluent 8*M* LiCl + 1*M* HCl.
C: Column 14 cm × 3·8 cm²; eluent 4*M* LiCl + 1*M* HCl.
D and E: Column 12·5 cm × 3·8 cm²; eluent 1*M* HCl.
Numbers refer to hydrolysis products of the compounds listed in Table II.

graph is given in Fig. 2A. The eluate fractions containing the $MePO(OH)_2$ and the $EtPO(OH)_2$ were treated separately with alkaline persulphate and vanadomolybdate to determine the MePO(OH)OMe and EtPO(OH)OEt, respectively, in the sample.

Group 3 contains MePO(OH)OPr, EtPO(OH)OEt and $HOPO(OEt)_2$. Upon hydrolysis, it yields $MePO(OH)_2$, $EtPO(OH)_2$ and H_3PO_4, respectively. It was treated exactly like Group 2 through the elution. Fig. 2B reveals that the elution separated $EtPO(OH)_2$ from the other phosphorus compounds but did not separate $MePO(OH)_2$ from H_3PO_4. The fraction containing $EtPO(OH)_2$ was treated with alkaline persulphate and vanadomolybdate to determine the original EtPO(OH)OEt. Aliquots of the fraction containing $MePO(OH)_2$ and H_3PO_4 were treated as in the analysis of Group 1. Thus each compound of this group was determined.

Group 4 contains EtPO(OH)OPr, PrPO(OH)OEt and HCl but no LiCl. The HCl was removed by vacuum evaporation. The residue was dissolved in 20 ml of 6*M* HCl and refluxed for 2·5 hr to convert the phosphorus compounds to $EtPO(OH)_2$ and $PrPO(OH)_2$. The hydrochloric acid was removed by vacuum evaporation. The residue was dissolved in 4*M* LiCl + 1*M* HCl. An aliquot was chromatographed at 50° through a column, 14 cm × 3·8 cm^2, of the low-capacity resin. Fig. 2C reveals that the two phosphonic acids were quantitatively separated. Each was determined by treatment with alkaline persulphate and vanadomolybdate as described above.

Group 5 contains MePO(OH)OBu, $HOPO(OPr)_2$ and BuPO(OH)OMe. Upon hydrolysis it yields $MePO(OH)_2$, H_3PO_4 and $BuPO(OH)_2$, respectively. The analysis of this group is like that of Group 4 up to the elution. Then a column, 19 cm × 3·8 cm^2. and 1*M* HCl were used. As in Group 3, the higher phosphonic acid is separated from the other phosphorus compounds (Fig. 2D) and is determined by treatment with alkaline persulphate and vanadomolybdate. The unseparated $MePO(OH)_2$ and H_3PO_4 were determined as in Group 2.

Group 6 contains BuPO(OH)OEt and EtPO(OH)OBu, yielding $BuPO(OH)_2$ and $EtPO(OH)_2$, respectively, on hydrolysis. The analysis was performed like that of Group 5 through the elution. Fig. 2E reveals that the separation of the two phosphonic acids was quantitative. Each was determined by treatment with alkaline persulphate and vanadomolybdate.

RESULTS AND DISCUSSION

One solution containing known concentrations of all 19 phosphorus compounds was analysed in triplicate. A similar solution was analysed in duplicate. These results

TABLE II.—ANALYSIS OF KNOWN MIXTURES

No.	Compound	Solution 1				Solution 2		
		Taken, *mmol*	Recovery, %			Taken, *mmol*	Recovery, %	
			1	2	3		1	2
1	H_3PO_4	0·0392	96	95	95	0·0594	98	97
2	$MePO(OH)_2$	0·0440	99	97	101	0·0630	103	101
3	MePO(OH)OMe	0·0080	105	108	101	0·0735	102	98
4	$HOPO(OMe)_2$	0·0321		104	106	0·0361	99	102
5	MePO(OH)OEt	0·0335	97	90	91	0·0520	88	90
6	EtPO(OH)OMe	0·0408		90	87	0·0635	86	86
7	MePO(OH)OPr	0·0362		89	89	0·0582	86	84
8	EtPO(OH)OEt	0·0192	95	95	92	0·0325	91	88
9	$HOPO(OEt)_2$	0·0395		89	88	0·0604	89	89
10	EtPO(OH)OPr	0·0390	102	87	98	0·0595	92	94
11	PrPO(OH)OEt	0·0406		91	94	0·0615	93	90
12	MePO(OH)OBu	0·0194		98	95	0·0320	95	96
13	$HOPO(OPr)_2$	0·0386	98	84	92	0·0585	97	92
14	BuPO(OH)OMe	0·0390		92	93	0·0612	95	96
15	BuPO(OH)OEt	0·0382	103	90	92	0·0592	93	93
16	EtPO(OH)OBu	0·0378		93	94	0·0587	98	95
17	PrPO(OH)OBu	0·0388	105	95	94	0·0606	99	100
18	BuPO(OH)OBu	0·0396	100	106	98	0·0618	97	96
19	$HOPO(OBu)_2$	0·0395	95	102	99	0·0612	98	96
Mean			100	94	95		95	94
Standard Deviation			4	6	5		5	5

are recorded in Table II. In the first analysis of solution 1, the individual compounds of the inseparable groups were not determined separately.

The table indicates that the accuracy and precision of the results are satisfactory for mixtures as difficult as these. In general, compounds 5, 6, 7, 8 and 9 show slightly lower recoveries than the others. The fact that these are the only compounds which were passed through the column of cellulose impregnated with zirconia indicates that incomplete desorption from the zirconia may account for low results. An application of the t-test revealed that the probability that the low results for these compounds are caused by chance alone is about one in four.

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Zusammenfassung—Eine Methode zur Bestimmung jeder Komponente in einer Mischung von 19 Säuren des Phosphors wird mitgeteilt.

Résumé—Les auteurs décrivent une méthode de dosage de chaque composé dans un mélange de 19 acides de phosphore.

REFERENCES

[1] K. C. Park, *Thesis*, Rutgers, The State University, New Brunswick, N.J., 1959.
[2] J. R. Van Wazer, *Phosphorus and Its Compounds*, Vol. I. Interscience Publishers, New York, N.Y., 1958.
[3] F. Jakob, *Thesis*, Rutgers, The State University, New Brunswick, N.J., 1960.
[4] F. Jakob, K. C. Park, J. Ciric and W. Rieman, *Talanta*, 1961, **8**, 431.
[5] W. Rieman and A. Breyer, *Chromatography: Columnar Liquid-solid Ion-exchange Processes* in *Treatise on Analytical Chemistry*, Part I, Vol. 3, edited by I. M. Kolthoff and P. J. Elving. Interscience Publishers, New York, N.Y., 1961.
[6] J. Beukenkamp, W. Rieman III and S. Lindenbaum, *Analyt. Chem.*, 1954, **26**, 505.
[7] H. Yurow, private communication.
[8] J. Kolmerten and J. Epstein, *Analyt. Chem.*, 1958, **30**, 1536.
[9] C. J. Barton, *ibid.*, 1948, **20**, 1068.

Talanta, 1962, Vol. 9, pp. 581 to 591. Pergamon Press Ltd. Printed in Northern Ireland

TITRIMETRIC ANALYSIS WITH CHLORAMINE-T—V*

TITRATIONS IN HYDROCHLORIC ACID MEDIA USING IODINE MONOCHLORIDE AS A REACTION INTERMEDIATE

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Summary—A critical appraisal has been made of the use of chloramine-T in conjunction with iodine monochloride as a reaction intermediate in Andrews-type titrations of arsenic^{III}, antimony^{III}, hydrazine, thiocyanate and thallium^{I}. Location of the end-point by potentiometric means and by several visual indicators has been examined over a very wide range of conditions. Optimum conditions for each determination have been established and have proved to be rather limited in most cases, severely so for antimony^{III}, while for hydrazine accurate results cannot be obtained under any conditions.

PRIOR to the present work, a solitary reference to the use of chloramine-T in Andrews-type reactions could be found. Berry[2] had titrated iodide under vaguely defined conditions to iodine monocyanide, with starch as indicator. He also titrated thallium^{I} in the presence of an excess of iodine monochloride at unspecified acidity with carbon tetrachloride as indicator. His results were reported to a rather low precision. During the course of this work Singh and Sood[3,4] reported a superficial examination of a number of determinations under apparently uniform, but rather ill-defined conditions using chloroform as indicator. Some of the determinations were made at suboptimum conditions. They have similarly reported[5,6] on the use of chloramine-B. A critical examination and delineation of reaction conditions is therefore to be desired.

A number of determinations have accordingly been examined at the highest volumetric precision over a wide range of conditions and by a number of techniques. The selection of determinations has been made (a) with a view to covering a representative cross-section of the possible reactions, (b) so that primary standard purity compounds or compounds of high purity easily and accurately assayed are available, and (c) to include the basic reaction with iodide,[1] the primary standards arsenic^{III} and hydrazine, reversible reactions—iodide and thallium^{I}, partially reversible reactions—arsenic^{III} and antimony^{III}, and irreversible reactions—hydrazine and thiocyanate, and some of the most useful reactions, particularly thiocyanate.

The substitution of chloramine-T for the more expensive potassium iodate in Andrews-type titrimetric reactions involves the addition of iodine monochloride as a reaction intermediate, and requires re-oxidation of reduction products of iodine monochloride by the titrant. The oxidation of iodide and the iodine to monopositive iodine ion in the hydrochloric acid media has been investigated over a wide range of conditions, and found to be perfectly stoicheiometric over only rather narrow limits of hydrochloric acid concentration.[1] However, the deviations from stoicheiometry in the normal working range with comparatively large quantities of iodide become much less

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significant when relatively small quantities of iodine monochloride are used as a reaction intermediate. Thus, though the determination of iodide is accurate only in 3·0–4·0*M* hydrochloric acid, when 2 ml of 0·1*M* iodine monochloride is used as a reaction intermediate the error is 0·01 ml or less in 1·0 to 5·0*M* hydrochloric acid, and for 5 ml the range is 2·0 to 4·0*M* hydrochloric acid for the same error. This does not, of course, include other errors which may arise in particular determinations. In fact for all five substances examined, under all of the conditions from 1·0 to 5·0*M* hydrochloric acid and 1·0 to 25·0 ml of 0·1*M* iodine monochloride, the titration error does not exceed 0·3%, with the single exception of potentiometric determination of thallium[I] in 5·0*M* hydrochloric acid and 5·0 ml of iodine monochloride, where the error is 0·4%. The error can be reduced to one tenth of this value by suitable choice of conditions except in the determination of hydrazine.

EXPERIMENTAL

Apparatus and reagents

Complete details have been given elsewhere;[7] the apparatus and most of the reagents and indicators have already been described.[8,9,10] The remaining reagents were as follows. Titration conditions refer to the end-point concentrations.

Antimony[III]*:* A 0·05*M* solution prepared from AnalaR potassium antimonyl tartrate after drying for 1 hr at 100°. The solution was standardised against ultimate standard 0·01667*M* potassium bromate in a medium 2*M* in hydrochloric acid and 0·1*M* in potassium bromide, both potentiometrically (factor 1·0035) and with rosaniline as visual indictor[8] (factor 1·003, 1·0035, 1·003).

Thallium[I]*:* A 0·05*M* solution prepared from AnalaR thallium sulphate. The solution was standardised by titration in 3·5*M* hydrochloric acid with primary standard 0·025*M* potassium iodate,[11,12] potentiometrically (factor 0·998), visually with carbon tetrachloride (factor 0·997, 0·997) and visually with amaranth (factor 0·9975, 0·9975).

Hydrazine sulphate: A 0·025*M* solution prepared from AnalaR hydrazine sulphate. The solution was check standardised against primary standard 0·025*M* potassium iodate by titration in 4*M* hydrochloric acid,[11,13] potentiometrically (factor 0·9904) and with the visual indicator amaranth (factor 0·991, 0·991, 0·991).

Thiocyanate: A 0·01667*M* solution prepared from AnalaR potassium thiocyanate after drying at 150° for 2 hr. The solution was standardised by titration in 4*M* hydrochloric acid with primary standard 0·025*M* potassium iodate,[11,14] potentiometrically (factor 1·0175), with the visual indicators amaranth (factor 1·0184, 1·0179) and carbon tetrachloride (factor 1·0175, 1·017, 1·017).

Iodine monochloride: A 0·1*M* solution in 5·0*M* hydrochloric acid was prepared by dissolving 7·12 g of AnalaR potassium iodate in warm water, adding 11·16 g of AnalaR potassium iodide to the cooled solution followed by 500 ml of 10*M* hydrochloric acid and dilution to 1 litre. Before use, a portion of this solution was titrated with 0·025*M* potassium iodate (or occasionally 0·1*M* potassium iodide) to the equivalence point using 10 ml of carbon tetrachloride as indicator.

Procedure

Carbon tetrachloride was used as the indicator for the extractive end-point, 5 ml being employed in a final volume of 100 ml, instead of chloroform which is more usual. The higher partition coefficient in the former solvent renders the titration slower, in the end-point region, but with an extended period of vigorous shaking between titrant increments in this region rather sharper and more accurate and precise end-points were achieved and considered desirable in the present appraisal.

Potentiometric and visual indicator titration methods have been described.[1,7–10] The concentrations recorded are those at the equivalence point. All determinations were replicated, but the potentiometric results recorded in Table II are those of the individual titrations illustrated in the figures: only the visual indicator results are means of triplicate determinations.

RESULTS AND DISCUSSION

Iodide

The direct titration of iodide to iodine monochloride has been examined.[1] From this work, the corrections shown in Table I have been calculated for customary additions of reaction intermediate at a range of concentrations of hydrochloric acid for both

potentiometric titration and visual indication using carbon tetrachloride. These corrections have been applied to the results given in Table I.

TABLE I

End-point location	Potentiometric			Carbon tetrachloride		
Volume of 0·1*M* ICl, *ml*	2·0	5·0	25·0	2·0	5·0	25·0
HCl concentration, *M*						
1·0	+0·008	+0·02	+0·10	+0·004	+0·01	+0·05
2·0	+0·006	+0·015	+0·075	+0·003	+0·01	+0·04
3·0	+0·004	+0·01	+0·05	+0·002	+0·005	+0·025
4·0	—	—	−0·01	+	+	+0·01
5·0	−0·014	−0·035	−0·175	+	+	+0·01

*Arsenic*III

By the use of iodine monochloride as a reaction intermediate, the direct titration of arsenic^{III} by the Andrews procedure becomes possible with chloramine-T, permitting replacement of the more expensive potassium iodate as the titrant. Furthermore, this procedure affords an additional means of standardising chloramine-T solutions not only against the primary standard arsenious oxide, but also indirectly against the ultimate standard potassium iodate as an alternative to the rather more complex route via iodine and thiosulphate.[8] This method is particularly advantageous for chloramine-T which is to be used in Andrews type determinations.

Potentiometric and carbon tetrachloride end-points are highly precise.

Using carbon tetrachloride indication, with 1 ml of 0·1*M* iodine monochloride the end-points were late in acid concentrations below 5*M*; with 2 ml of reaction intermediate the results were high in acid concentrations of 2*M* or less, but highly accurate in 3*M* or higher concentrations, with an amount of reaction intermediate (25 ml of 0·1*M*) equivalent to the total amount of reductant no significant error is introduced in 4*M* acid. A hydrochloric acid concentration of 3–5*M* with 2 ml of 0·1*M* iodine monochloride gives optimum results.

Using amaranth[9] (0·2 ml per 100 ml) or *p*-ethoxychrysoïdine[9] (0·3 ml per 100 ml), added about 0·1–0·2 ml prior to the equivalence point, the colour changes from pink to the pale yellow of iodine monochloride. The end-points are late, particularly with *p*-ethoxychrysoïdine which shows no signs of reversibility in this titration, and neither indicator can be recommended for other than rough work.

Potentiometric titration (Fig. 1) in 1–5*M* hydrochloric acid using 2 ml of 0·1*M* iodine monochloride gives accurate results and affords a rapid, pleasing and convenient method of determination. The potentials are highly reproducible and attain equilibrium, even in the equivalence-point region, very quickly. This is the best method for potentiometric titration of arsenic^{III} with chloramine-T. The titration in 3*M* acid using 1 ml of reaction intermediate confirms that carbon tetrachloride indication does give a late end-point under these conditions, and the results in general show that the errors with visual indicators are properly attributed to the indicators themselves and not to the reaction.

*Antimony*III

Carbon tetrachloride proved to be unusable as an indicator, no purple colour being

produced in the solvent layer before the equivalence point. The same phenomenon has been observed with potassium iodate as titrant by Smith and Willcox.[11] The interference is ascribed to the tartaric acid liberated on acidification of the tartrate complex. In the absence of tartaric acid, solvent extraction indication is feasible.[15]

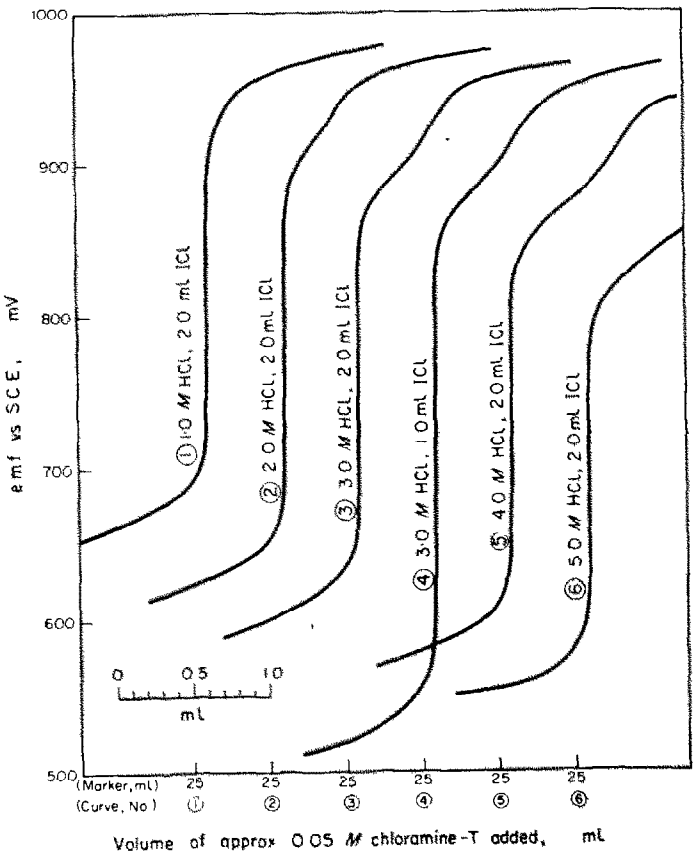


FIG. 1.—Titration of 25-ml aliquots of approx. $5 \times 10^{-2}M$ arsenic^{III} diluted to an equivalence point volume of 200 ml, with approx. $5 \times 10^{-2}M$ chloramine-T.

Amaranth, with a colour change from orange-pink to pale yellow, gives accurate results over the range of conditions recorded in Table II, with 2–5 ml of $0{\cdot}1M$ iodine monochloride and a hydrochloric acid concentration of $3M$ as optimum. In $4M$ acid, the colour faded appreciably prior to the end-point, while in $2M$ acid the end-point was not sharp because either of hydrolysis of the iodine monochloride or of slowness of reaction (*vide infra*).

The results of the potentiometric titrations (Fig. 2) are in substantial agreement with the amaranth figures, and confirm that the optimum acid concentration is $3M$. At $2M$, the reaction is distinctly slow, the potentials requiring 6 min to reach equilibrium in the equivalence point region, and at $4M$, the Sb^{V}/Sb^{III} potential is sufficiently elevated to offset the tail potentials, offering an explanation of the fading end-points with amaranth.

The range of acid concentration within which accuracy is maintained is rather

TABLE II.—TITRATIONS WITH CHLORAMINE-T USING IODINE MONOCHLORIDE AS A REACTION INTERMEDIATE

Equivalence point conditions		End-points,[a] ml of 0·05*M* chloramine-T						
					Visual Indicators			
Concn. of HCl, *M*	Vol. of 0·1*M* ICl, *ml*	Calculated	Potentiometric	Error[b]	CCl_4[c]	Error[b]	Amaranth[d]	Error
Iodide					Iodide			
1·0	nil	39·94	39·85	−0·09	39·90	−0·04		
2·0	nil		39·88	−0·06	39·91	−0·03		
3·0	nil		39·91	−0·03	39·92	−0·02		
4·0	nil		39·95	+0·01	39·93	−0·01		
5·0	nil		40·08	+0·14	39·93	−0·01		
Arsenic^{III}					Arsenic^{III}			
1·0	2·0	25·11	25·10	0	25·16	+0·05		
2·0	2·0		25·11	+0·01	25·12	+0·01		
3·0	1·0		25·10	0	25·17	+0·06		
3·0	2·0		25·10	−0·01	25·11	0	25·15	+0·04
3·0	2·0						25·18[e]	+0·07
4·0	1·0				25·17	+0·06		
4·0	2·0		25·11	0	25·11	0	25·14	+0·03
4·0	2·0						25·17[e]	+0·06
4·0	25·0				25·11	+0·01		
5·0	1·0				25·11	0		
5·0	2·0		25·10	−0·02	25·11	0		
Antimony^{III}					Antimony^{III}			
2·0	2·0	23·81	23·82	+0·02	[f]		23·82	+0·01
3·0	2·0		23·805	0			23·81	0
3·0	5·0		23·82	+0·01			23·81	0
4·0	2·0		23·87	0			23·79	−0·02
Thallium^{I}					Thallium^{I}			
3·0	5·0	24·82	24·80	−0·01	24·81	0		
4·0	5·0		24·80	−0·03	24·81	−0·01		
4·0	25·0		24·75	−0·08	24·81	0		
5·0	5·0		24·82	−0·03	24·81	−0·01		
Hydrazine					Hydrazine			
3·0	2·0	23·52	23·57	+0·05	23·57	+0·05	23·56	+0·04
3·5	5·0		23·55	+0·03				
4·0	2·0		23·55	+0·03	23·55	+0·03	23·56	+0·04
4·0	5·0				23·59	+0·07		
4·0	25·0		23·58	+0·05	23·58	+0·07		
5·0	2·0		23·56	+0·03	23·57	+0·05	23·57	+0·05
Thiocyanate					Thiocyanate			
3·0	2·0	25·31	25·31	0	25·31	0	25·40	+0·09
3·0	5·0		25·31	+0·01	25·31	0		
4·0	2·0		25·31	0	25·31	0	25·40	+0·09
4·0	5·0		25·30	−0·01	25·31	0	25·39	+0·08
4·0	25·0		25·275	−0·04	25·31	+0·01		
5·0	2·0		25·32	0	25·31	0	25·40	+0·09
5·0	5·0		25·29	−0·05	25·31	0		

[a] The potentiometric results are the end-points of the titrations recorded in the figures. Other end-points are means of three replications.

[b] The errors for potentiometric and carbon tetrachloride end-points have been corrected for the iodine monochloride error given in Table I.

[c] 5·0 ml of carbon tetrachloride was used for a final titration solution volume of 100 ml.

[d] 0·2 ml of 0·1% aqueous amaranth for a final titration solution volume of 100 ml.

[e] Results for p-ethoxychrysoïdine. 0·3 ml of 0·1% aqueous solution of indicator for a final titration solution volume of 100 ml.

[f] Carbon tetrachloride cannot be used as an indicator in the presence of tartrate.

sharply delineated. For the visual indicator amaranth, the range is about 2·5 to 3·5*M*, for potentiometric titration it is about 2·5 to 4*M*. These ranges may be compared with those determined for potassium iodate as titrant by Hammock *et al.*[15] as 2·5–3·5*M* and by Mutschin[16] as 1·8–3·6*M*.

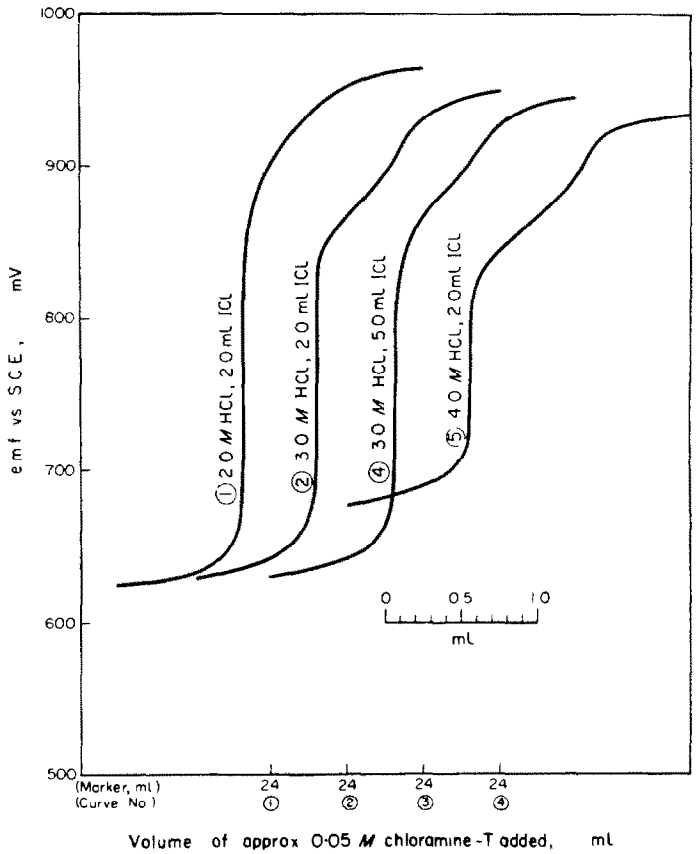


FIG. 2.—Titration of 25-ml aliquots of approx. $5 \times 10^{-2}M$ antimony^{III} diluted to an equivalence point volume of 200 ml, with approx. $5 \times 10^{-2}M$ chloramine-T.

Thallium^{I}

The formation and slow redissolution of a precipitate of thallium^{I} chloride slows the reaction sufficiently to preclude the use of colour indicators, but carbon tetrachloride is a precise and effective indicator, giving satisfactory results in the range 3–5*M* hydrochloric acid and 5 to 25 ml of reaction intermediate. The titration with iodate was found to be more rapid than that with chloramine-T and iodine monochloride.

Potentiometric titrations (Fig. 3) give accurate results in 3–4*M* hydrochloric acid with 5 ml of reaction intermediate, but reveal a negative error if the acid concentration is increased to 5*M* or if the amount of iodine monochloride is increased to 25 ml of 0·1*M*. Equilibration of the potentials was rapid throughout.

Reaction in the presence of iodine monochloride provides the only accurate method for the direct titration of thallium^{I} with chloramine-T, as will be demonstrated in a later paper.

Hydrazine

Hydrazine sulphate being a primary grade standard substance, and being titratable to high accuracy with bromate[17] and iodate[11,13], hopes were entertained of a similar favourable reaction with chloramine-T and iodine monochloride, thus providing another alternative means of standardisation. Although the end-points are sharp and precise, and the results are reproducible and consistent between the various methods

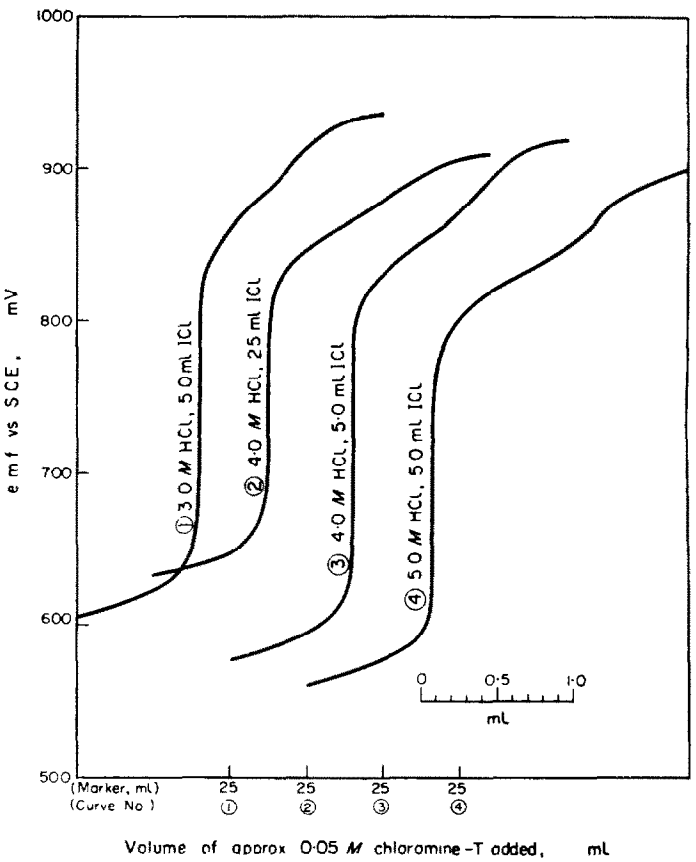


FIG. 3.—Titration of 25-ml aliquots of approx. $5 \times 10^{-2}M$ thallium[I] diluted to an equivalence point volume of 200 ml, with approx. $5 \times 10^{-2}M$ chloramine-T.

of indication, there is a positive error of 0·15 to 0·2%, and so the method must be rejected as a means of standardisation. With the application of the appropriate correction deduced from Table II, the method does give an accuracy of about $\pm$ 0·05% which is adequate for routine applications.

Over the full range of conditions reported in Table II, potentiometric and visual indication with both carbon tetrachloride and amaranth give satisfactory results, with a slight advantage in favour of 2 ml of 0·1*M* iodine monochloride and 3*M* hydrochloric acid. Potentials rapidly attained equilibrium and the potentiometric method is considered to be best of all the methods investigated for this determination. Titration curves are shown in Fig. 4.

Thiocyanate

The facile and highly accurate determination by the Andrews method of thiocyanate and of many important metals such as copper, mercury and zinc, through their compounds or complexes with thiocyanate render this one of the most important applications of iodate titrimetry.

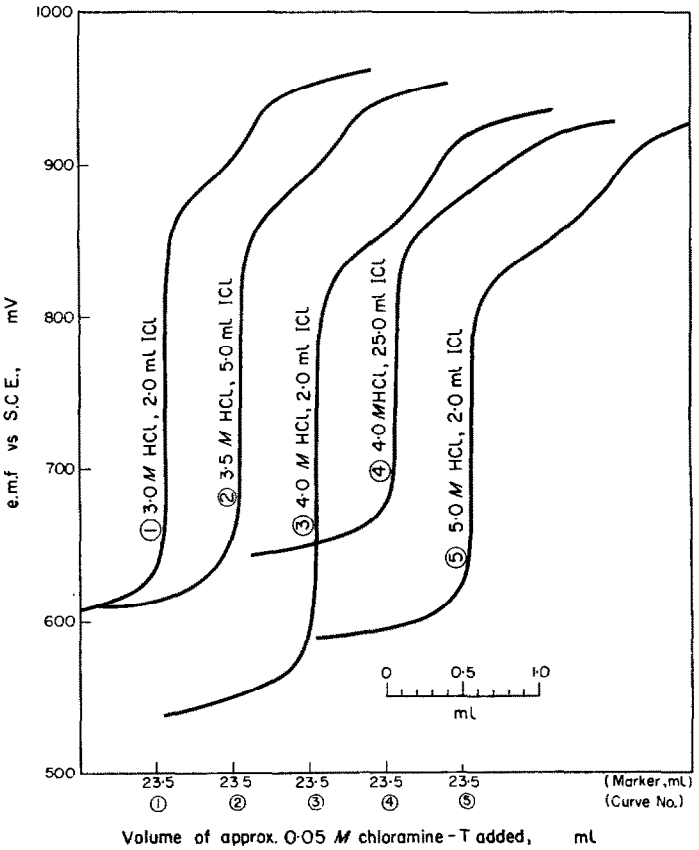


FIG. 4.—Titration of 25-ml aliquots of approx. $2{\cdot}5 \times 10^{-2}M$ hydrazine diluted to an equivalence point volume of 200 ml, with approx. $5 \times 10^{-2}M$ chloramine-T.

With chloramine-T as titrant, carbon tetrachloride yields sharp end-points and highly accurate results in 3–5*M* hydrochloric acid and with 2–25 ml of reaction intermediate, though in 3*M* acid the violet colour of iodine in the solvent globule was very faint until quite close to the end-point.

The poor colour change of amaranth and the high positive indicator error do not commend this indicator.

The potentiometric titrations (Fig. 5) are precise and accurate with moderate amounts of reaction intermediate, but appreciable negative errors arise with large amounts of iodine monochloride. Equilibration of potentials is rather less rapid than in some other determinations, but is quite satisfactorily fast.

Overall, 2–5 ml of 0·1*M* iodine monochloride and an equivalence point concentration of 4*M* hydrochloric acid are recommended. Chloramine-T compares favourably with iodate in this useful determination.

The Second Potentiometric Inflection

Except at very low hydrochloric acid concentrations, all of the potentiometric curves show evidence of a second small inflection at high potentials. The existence of this inflection has previously been noted.[9] No sign of this phenomenon has been detected other than potentiometrically and in high hydrochloric acid concentrations in the absence of other free halides. In the titration of iodide with permanganate, such an inflection has been correctly ascribed[18] to oxidation to iodate, but early tentative

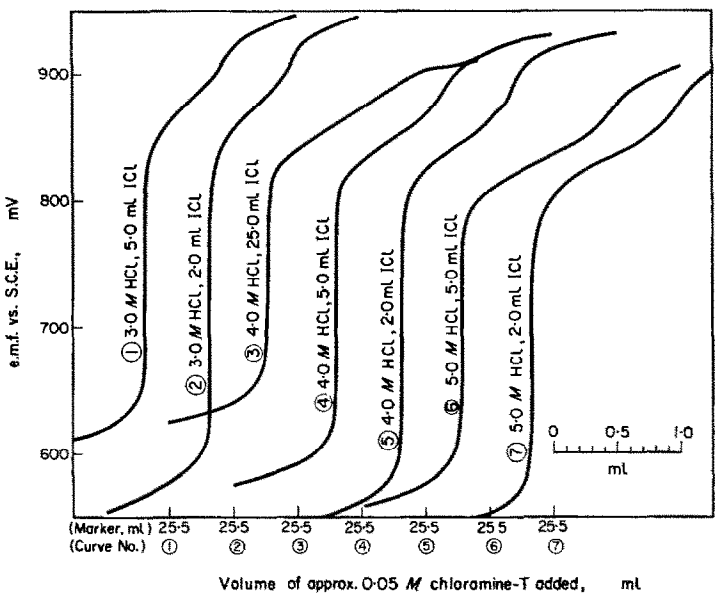


FIG. 5.—Titration of 25-ml aliquots of approx. $1{\cdot}667 \times 10^{-2}M$ thiocyanate diluted to an equivalence point volume of 200 ml, with approx. $5 \times 10^{-2}M$ chloramine-T.

indications[19] that chloramine-T could oxidise iodine to iodate at pH 7–9 proved illusory,[1,7] and the indications were traced to hydrolysis of iodine to hypo-iodite and iodide. In high acid concentrations, the oxidation is even less likely, nor do the potentials or inflections agree with such a hypothesis. Nor can the reaction be oxidation of I^+ to I^{3+} since the inflections occur much too early and, moreover, the inflections have been observed in media free from iodine and iodine monochloride.[9] The inflections are not all regular, as the values in Table III show, but they do appear to be independent of the iodine monochloride concentration, and to increase with increasing hydrochloric acid concentration according to the equation:

$$\Delta = 0{\cdot}24[\mathrm{HCl}] - 0{\cdot}17$$

where Δ is the difference in ml between the main and second inflections. The cause of this is obscure. It may be caused by a change of redox system after the addition of a certain amount of excess oxidant, but no satisfactory change has yet been formulated, and at such concentrations the activation energy of charge transfer at the electrode surface should have no effect and, as has been said, potential changes reach equilibrium very rapidly. The most reasonable explanation seems to be the existence of some impurity in the hydrochloric acid which is oxidisable only at very high potentials,

but no identification has been possible. Whatever it is, there is abundant evidence that it does not affect the analytical accuracy of determinations by chloramine-T titrimetry.

TABLE III.—THE SECOND INFLECTION IN POTENTIOMETRIC CHLORAMINE-T TITRATIONS IN THE PRESENCE OF IODINE MONOCHLORIDE

Concentration of HCl, *M*	Volume of 0·1*M* ICl used, *ml*	Δ, *ml*	Mean Δ, *ml*
1	2	—	—
2	2	0·4	0·4
3	1	0·55	
3	2	0·52	0·54
3	5	0·56	
3·5	5	0·65	0·65
4	2	0·76	
4	5	0·90	0·79
4	25	0·74	
5	2	0·99	1·03
5	5	1·10	

The volume difference Δ in ml between the two inflections is given as the mean of all the determinations employing the specified conditions, and illustrated in the figures.

CONCLUSIONS

Chloramine-T with the assistance of iodine monochloride as a reaction intermediate affords a convenient substitute for potassium iodate. The titrimetric precision and accuracy in the reactions examined are of the same order as with potassium iodate. In view of the experience, particularly with hydrazine and antimony, caution must be exercised in any attempt to generalise, and it is desirable that other reactions should be checked against the iodate method before being accepted, but the reactions chosen have been reasonably representative of the whole. Again with caution, it could be deduced that the use of 2–5 ml of 0·1*M* iodine monochloride and an equivalence point concentration of 3–4*M* hydrochloric acid generally gives the best results.

The rapid equilibration and the reproducibility of the potentials make the potentiometric method attractive, and the results under the correct conditions are accurate. Carbon tetrachloride as an extractive solvent gives very accurate results, though the iodine colour in the solvent layer is often weak, and this indicator cannot be used in the presence of tartaric acid. It is essential that adequate amounts of reaction intermediate and hydrochloric acid be present. Except, fortunately, in the determination of antimony, amaranth and *p*-ethoxychrysoïdine have little advantage. The colour changes are poor and the errors positive and rather high.

The range of conditions giving accurate results is generally rather restricted, more so for the potentiometric method than with extractive indicators, calling for the exercise of some care, particularly in the determination of antimony. This situation is not peculiar to chloramine-T.

Analysis and interpretation of the potentiometric curves will be deferred to a later paper, but it may presently be noted that the curves attest to two-electron transfer, to the anagenic effect of iodine monochloride and the katagenic effect of chloride ion, and to a change in molecular complexity during reaction.

Zusammenfassung—Eine kritische Untersuchung für die Anwendung von Chloramin-T im Zusammenhang mit Jodmonochlorid als Zwischenprodukt in Titrationen nach Andrews von As(III), Sb(III), Hydrazin, Rhodan und Tl(I) wurde durchgeführt. Die Festlegung des Endpunktes erfolgte sowohl potentiometrisch als auch mittels verschiedener visueller Indikatoren und wurde über einen weiten Bereich von Milieuänderungen untersucht. Die optimalen Bedingungen für jede Titration wurden ermittelt; sie liegen alle ziemlich enge, besonders für Sb(III), während Hydrazin unter keinen Bedingungen genau bestimmt werden konnte.

Résumé—Les auteurs ont fait une estimation critique de l'utilisation de la chloramine-T en liaison avec le monochlorure d'iode comme réaction intermédiaire dans les titrages, du type Andrews, de l'arsenic(III), de l'antimoine (III), de l'hydrozine, du thiocyanate et du thallium(I). La détermination du point équivalent par potentiométrie et par différents indicateurs visuels a été étudiée dans un très grand domaine de conditions. Les conditions les meilleures ont été établies pour chaque dosage et se sont révélées assez limitées dans la plupart des cas, assez rigoureusement pour l'antimoine(III), alors que, pour l'hydrazine, des résultats précis ne peuvent être obtenus dans aucune condition.

REFERENCES

[1] E. Bishop and V. J. Jennings, *Talanta*, 1960, **8**, 697.
[2] A. J. Berry, *Analyst*, 1934, **55**, 736.
[3] B. Singh and K. C. Sood, *Analyt. Chim. Acta*, 1955, **13**, 301.
[4] *Idem, ibid.*, 1955, **13**, 305.
[5] *Idem, ibid.*, 1954, **11**, 313.
[6] *Idem, ibid.*, 1954, **11**, 315.
[7] V. J. Jennings, *Titrimetric Analysis with Chloramine-T*, Univ. Exon., 1957.
[8] E. Bishop and V. J. Jennings, *Talanta*, 1958, **1**, 197.
[9] *Idem, ibid.*, 1961, **8**, 22.
[10] *Idem, ibid.*, 1961, **8**, 34.
[11] G. F. Smith and C. S. Wilcox, *Ind. Eng. Chem., Analyt.*, 1942, **14**, 49.
[12] E. H. Swift and C. S. Garner, *J. Amer. Chem. Soc.*, 1936, **58**, 113.
[13] B. Singh and I. Ilani, *J. Indian Chem. Soc.*, 1937, **14**, 376.
[14] R. Gaugin, *Analyt. Chim. Acta*, 1949, **3**, 272.
[15] E. W. Hammock, R. A. Brown and E. H. Swift, *Analyt. Chem.*, 1948, **20**, 1048.
[16] A. Mutschin, *Z. analyt. Chem.*, 1936, **106**, 1.
[17] E. Bishop, *Analyst*, 1960, **85**, 422.
[18] *Idem, ibid.*, 1953, **78**, 149.
[19] E. Bishop and D. Parrish, unpublished work; D. Parrish, Thesis, Univ. Dunelm., 1948.

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TITRIMETRIC ANALYSIS WITH CHLORAMINE-T—VI*

THE CHLORAMINE-T–ANTIMONY^{III} REACTION

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Summary—A critical investigation has been made of the determination with chloramine-T of antimony^{III} under a wide range of conditions in hydrochloric acid, sulphuric acid and buffer media in the presence and absence of varied concentrations of halide ion and complexing agent by the potentiometric method. A wide variety of reversible and irreversible indicators has also been examined for usefulness under these conditions. Accurate determinations are possible by potentiometric titration in 1–4*M* hydrochloric acid and using amaranth as indicator in 1–3*M* hydrochloric acid. Several other indicators are useful in 2*M* hydrochloric acid. Both potentiometric and visual indicator methods give late end-points in the presence of bromide, but sulphuric acid with or without added halide is an unsuitable medium. Titration in adequately buffered media of pH 6·5–7·5 in the presence of 5×10^{-4} to 5×10^{-3}*M* iodide gives excellent results and is probably the best method. In 3*M* hydrochloric acid with the addition of 2–5 ml of 0·1*M* iodine monochloride, satisfactory results are given using either amaranth or potentiometry to locate the end-point but the conditions are critical.

The reactions of chloramine-T with arsenic^{III} have been subjected to detailed and extensive investigation,[2,3] and it has been demonstrated that chloramine-T can be directly substituted for potassium bromate or iodine in the determination of arsenic^{III} under the appropriate conditions. It has further been shown[1] that chloramine-T can be substituted for potassium iodate in the same determination if iodine monochloride is used as reaction intermediate. It was hoped that antimony^{III} would be similarly amenable to determination with this reagent.

Earlier literature has been criticised on several counts,[4] and accounts of the chloramine-T-antimony^{III} reaction are no exception, being characteristically vague. Chloramine-T has been used to titrate antimony^{III} in a bicarbonate solution of unspecified strength containing a "little" iodide and "some" tartaric acid[5] using starch as indicator, in 1*M* hydrochloric acid at an elevated but undefined temperature,[6] at room temperature in hydrochloric acid of unspecified concentration[7] by the potentiometric method, in 1*M* hydrochloric acid at an "elevated" temperature with methyl red as indicator,[8] and in 5% concentrated hydrochloric acid ($? \sim 0{\cdot}6M$) at room temperature with brilliant carmoisine as indicator.[8] No investigation of conditions has been reported.

The reactions of antimony^{III} may be expected strongly to parallel those of arsenic^{III} with differences arising from the lower electronegativity of the Period V element and the consequent shift of stability towards the lower oxidation state. In particular, three factors will produce differences in behaviour from arsenic: the higher (0·17 V) oxidation potential of the Sb^{III}/Sb^{V} system enhanced by the presence of tartrate, the decreased solubility of hydrolysis products of both states, and the greater ease of

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complex formation. Thus, experience predicted that complexation and sparing solubility in sulphuric acid media would be troublesome. All these expectations were fulfilled during the investigation.

Although the conditions for quantitative reaction with arsenic are wide, they are sharply defined at the extremities,[2,3] so a similarly wide range of conditions has been investigated by the potentiometric method for antimony, in order precisely to delimit them. Arsenic is determinable with bromate under a wide range of conditions, again sharply delimited,[9] but during an extensive investigation of bromate titrimetry,[9] a curious phenomenon was encountered with antimony.[2] Positive errors were encountered in extremes of acidity as with arsenic, both in the presence and absence of bromide, but with antimony a marked deviation in the opposite sense was found in the absence of added bromide within the acidity range of approximately 0·2–1·0*M* acid, the sign of error reversing again at the lower limit. This region of reaction has been submitted to kinetic examination.[10] Stepwise coverage of the acid conditions has, therefore, been included in the present investigation to discover whether a similar phenomenon exists in chloramine-T titrimetry.

The dearth of visual indicators for this determination is evident form the literature survey, and none of those proposed has been checked potentiometrically. A number of reversible and irreversible indicators have been developed for use in chloramine-T titrimetry and have been tested in the arsenic^{III} reaction,[3] and compared with potentiometric titrations[2] in order to define the indicator errors. The application of these indicators to the antimony determination has also been investigated and the results compared with potentiometric titrations.

Finally, the ease of hydrolysis of antimony compounds and the sparing solubility and slow reaction of the hydrolysis products requires in many conditions the addition of a complexing agent, of which the most popular is tartaric acid, in order to make reaction feasible. No investigation of the effects of such additions has been reported. Furthermore, though it is possible to use high purity antimony metal for solution preparation, the solutions emerge with slightly indeterminate acid concentrations, and the presence of unknown amounts of oxide with the metal still necessitates standardisation of the solution. Consequently, the antimonyl tartrate complex was used for preparing solutions and the influence of tartrate concentration was investigated.

Determination in high hydrochloric acid concentrations with the aid of iodine monochloride as a reaction intermediate, by the Andrews process, has already been reported.[1] Accurate results by potentiometric titration or by the use of amaranth as an internal indicator can be obtained, but only within rather narrow limits of hydrochloric acid concentration. Solvent extraction indication cannot be used in the presence of tartrate.

EXPERIMENTAL

Apparatus and reagents

Quantitative balances and glass-ware and the instruments for potentiometry have been described,[4] and the methods of preparation and standardisation of quantitative solutions have been given.[1–4,11] Other reagents, indicators and buffer solutions have been specified.[1–4,11] The tartaric acid used was AnalaR.

Procedures

Full details have been given,[12] and the methods for potentiometric[2] and visual indicator[3,4] titrations have been described. Titrimetric manipulative procedures have been discussed.[12,13] Concentrations quoted refer to the equivalence point volume, 100 ml for visual indicator titrations and 200 ml for potentiometric titrations.

RESULTS AND DISCUSSION

1. *Reaction in hydrochloric acid*

(*a*) *Potentiometric titration.* Curves are shown in Fig. 1 for titrations in 0·25–4·0*M* hydrochloric acid with or without the addition of further quantities of tartaric acid. Pre-end-point potentials were unsteady and became more unsteady with additional

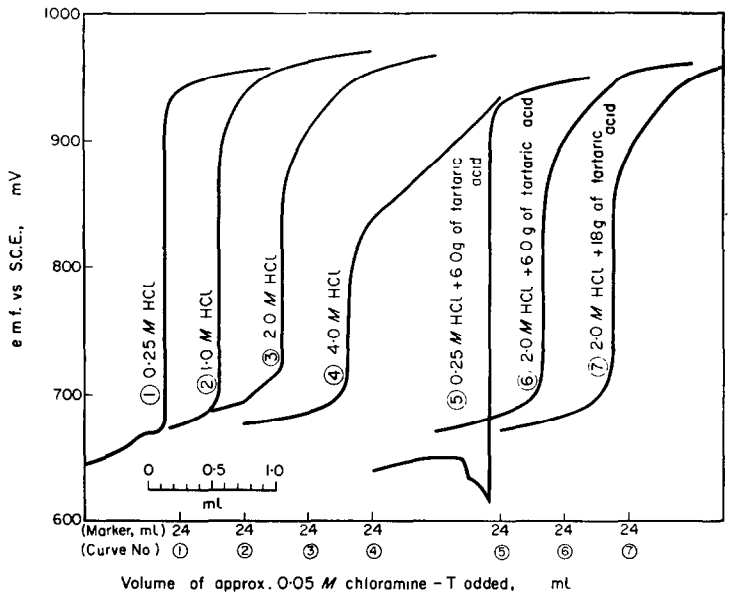


FIG. 1.—Direct titration with approx. $5 \times 10^{-2}M$ chloramine-T of 25-ml aliquots of approx. $5 \times 10^{-2}M$ antimonyl tartrate in hydrochloric acid media at an equivalence point volume of 200 ml.

tartaric acid. The reactions in 0·25*M* hydrochloric acid were very slow. Post-end-point potentials equilibrated rapidly. The results in Table I show that the titrations are accurate in 1–4*M* hydrochloric acid in the absence of additional tartaric acid, but below 1·0*M* positive errors occur which are enhanced by the addition of tartaric acid which also leads to late end-points in higher acid concentration, the effect increasing with increasing tartaric acid concentration.

In 1–4*M* hydrochloric acid, therefore, the chloramine-T-antimony^{III} reaction is stoicheiometric, but the addition of more than 6% of tartaric acid causes small positive errors.

(*b*) *Visual indicators.* Amaranth was examined as a visual indicator over the full range of hydrochloric acid concentration; the results are shown in Table I. The titration is accurate over the range of 1–3*M* hydrochloric acid, but outside this range the end-points are late as shown for 0·5 and 4·0*M* acid. In 0·25*M* acid, there was merely a slow fading of the colour with no definite end-point.

Since 2·0*M* hydrochloric acid proved satisfactory in both potentiometric and amaranth titrations, this condition was selected for examination of other indicators; results are given in Table I. Quinoline yellow and *o*-dianisidine changed colour prematurely and were therefore unsuitable. Methyl orange and tartrazine gave satisfactory colour changes, but the end-points are late by more than 0·1%. *p*-Ethoxychrysoïdine

gave fairly accurate results, but the colour change is not satisfactory. Neither tartrazine nor *p*-ethoxychrysoïdine showed reversibility after the first colour change. Bordeaux alone gave both a satisfactory colour change and accurate results. Methyl red[8] proved unsatisfactory since its normal pink colour changed to yellow early in the titration.

TABLE I.—TITRATION OF ANTIMONY^{III} IN HYDROCHLORIC ACID MEDIA WITH APPROX. 0·05*M* CHLORAMINE-T

HCl concentration, *M*	Potentiometric end-point *ml*	Potentiometric error %	Indicator	Indicator end-point *ml*	Indicator error %
0·25	23·89	+0·34	Amaranth	none	
0·5	—		Amaranth	23·88	+0·29
1·0	23·81	0	Amaranth	23·81	0
2·0	23·81	0	Amaranth	23·81	0
3·0	—		Amaranth	23·82	+0·04
4·0	23·82	+0·04	Amaranth	23·87	+0·21
0·25 + 6g tartaric acid	23·92	+0·46			
2·0 + 6g tartaric acid	23·84	+0·13			
2·0 + 18g tartaric acid	23·88	+0·29			
2·0			Methyl orange	23·84	+0·13
2·0			Methyl red	none	
2·0			Bordeaux	23·81	0
2·0			*p*-Ethoxychrysoïdine	23·82	+0·04
2·0			Quinoline yellow	none	
2·0			*o*-Dianisidine	none	
2·0			Tartrazine	23·85	+0·17

Calculated equivalence point, 23.81 ml.

Amaranth and bordeaux are recommended as indicators for the titration of antimony^{III} in 1·0–3·0*M* hydrochloric acid with chloramine-T. Tartrazine, *p*-ethoxychrysoïdine and methyl orange may also be used.

2. *Reaction in sulphuric acid*

Titrations in 0·125, 1·0 and 2·0*M* sulphuric acid using amaranth as indicator were unsuccessful. Even after 2 hr standing with a 0·2-ml excess of chloramine-T the solutions still retained the pink colour of the indicator. Attempted potentiometric titrations in 1·0 and 2·0*M* sulphuric acid confirmed the conclusion that the reaction is too slow to be of analytical use. Even with an excess of titrant present, the potentials continued to drift for many hr.

3. *Reaction in hydrochloric acid containing bromide*

(*a*) *Potentiometric titration.* Titration curves for 0·1*M* bromide over a range of hydrochloric acid concentrations are shown in Fig. 2. The results in Table II show that the end-points are all late, and that the addition of tartaric acid (Fig. 3, curve 5) does not enhance the error. Curves for 0·01*M* bromide are shown in Fig. 3, together with a set of curves at 2·0*M* hydrochloric acid for 0·01*M* bromide, 0·1*M* bromide and 0·1*M* bromide plus 6 g of tartaric acid so that the effects may be compared. Pre-end-point potentials were unsteady. After the end-point, equilibration was rapid and the colour of liberated bromine appeared within 0·05 ml past the end-point. The results

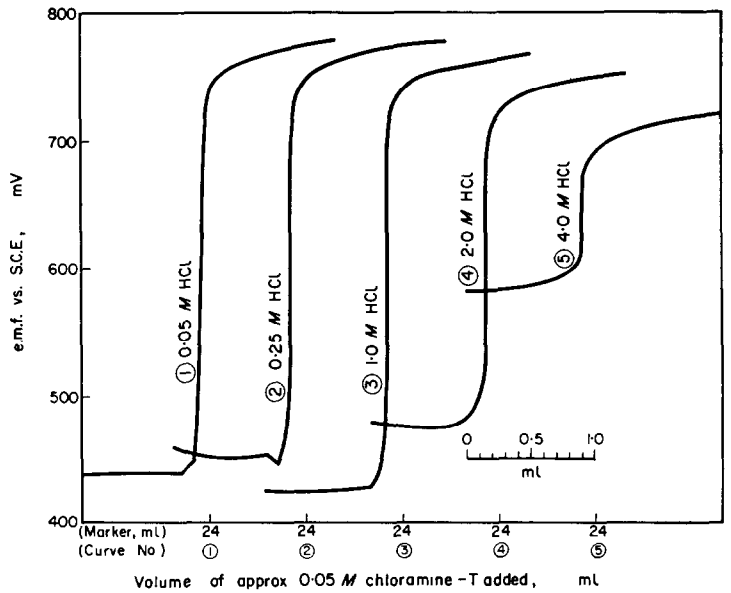


FIG. 2.—Direct titration with approx. $5 \times 10^{-2}M$ chloramine-T of 25-ml aliquots of approx. $5 \times 10^{-2}M$ antimonyl tartrate in hydrochloric acid media $0{\cdot}1M$ in bromide at an equivalent point volume of 200 ml.

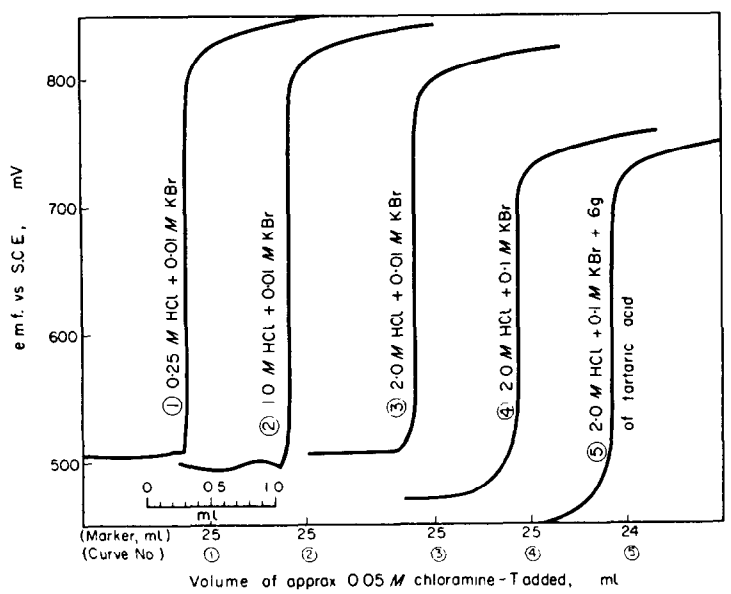


FIG. 3.—Direct titration with approx. $5 \times 10^{-2}M$ chloramine-T of 25-ml aliquots of approx. $5 \times 10^{-2}M$ antimonyl tartrate in hydrochloric acid-bromide media under various conditions at an equivalence point volume of 200 ml.

show that, while still high, the results are improved by the increase of potential caused by the ten-fold reduction in bromide concentration.

Reaction in hydrochloric acid in the presence of bromide is subject to positive

TABLE II.—TITRATION OF ANTIMONY^{III} IN HYDROCHLORIC ACID-BROMIDE MEDIA WITH APPROX. 0·05*M* CHLORAMINE-T

Concentrations, *M*		Equivalence point, *ml*	Potentiometric end-point error		Rosaniline end-point error	
HCl	KBr		*ml*	%	*ml*	%
0·05	0·1	23·81	23·93[a]	+0·50	—	—
0·25	0·1	23·81	23·88[a]	+0·29	none	—
0·25	0·01	24·81	24·82[b]	+0·04	24·82	+0·04
0·5	0·1	24·81	—	—	24·84	+0·12
0·5	0·01	24·81	—	—	24·82	+0·04
1·0	0·1	23·81	23·88[a]	+0·29		
		24·81			24·83	+0·08
1·0	0·01	24·81	24·86[b]	+0·20	24·83	+0.08
2·0	0·1	23·81	23·89[a]	+0·34		
		24·81	24·90[b]	+0·36	24·83	+0·08
2·0	0·1					
+6g tartaric acid		23·81	23·88[b]	+0·29		
2·0	0·01	24·81	24·85[b]	+0·16	24·82	+0·04
4·0	0·1	23·81	23·90[a]	+0·38	—	—

[a] see Fig. 2.
[b] see Fig. 3.

errors and cannot, therefore, be recommended. This is in sharp contrast to the high accuracy of the determination with bromate under similar conditions.[9]

(*b*) *Rosaniline as visual indicator.* Titrations conducted by the method described[4] for arsenic^{III} in 0·01 and 0·1*M* bromide over a range of concentrations of hydrochloric acid, using rosaniline hydrochloride as indicator, gave the results shown in Table II. The accuracy of *ca.* 0·05 to 0·1% is more apparent than real, because the appearance of the purple colour at the end-point was not sharp, though it was sharper in 0·01*M* than in 0·1*M* bromide. No definite end-point could be located in 0·25*M* acid with 0·1*M* bromide. This again is in sharp contrast to the bromate titration.[9]

4. *Reaction in sulphuric acid containing bromide*

(*a*) *Potentiometric titration.* Titration curves for 0·1*M* bromide over a range of sulphuric acid concentrations are shown in Fig. 4. The results in Table III show that the end-points are late and the shapes of the curves indicate that the end-points are not

TABLE III.—POTENTIOMETRIC TITRATION OF ANTIMONY^{III} IN SULPHURIC ACID CONTAINING POTASSIUM BROMIDE WITH APPROX. 0·05*M* CHLORAMINE-T

Conditions, *M*		Calculated end-point, *ml*	Determined end-point, *ml*	Error %
H_2SO_4	KBr			
0·125	0·1	23·81	23·88	+0·29
1·0	0·1	23·81	23·88	+0·29
2·0	0·1	23·81	23·95	+0·36
1·0	0·01	24·81	24·87	+0·24
1·0	0·1	24·81	24·88	+0·28

sharp. Increase of the bromide/bromine potential by lowering the bromide concentration to 0·01*M* gave some improvement, but the end-point remains late. A pair of

curves in 1*M* sulphuric acid and 0·1 and 0·01*M* bromide is included in Fig. 4 by way of illustration. The results are similar to those with hydrochloric acid plus bromide.

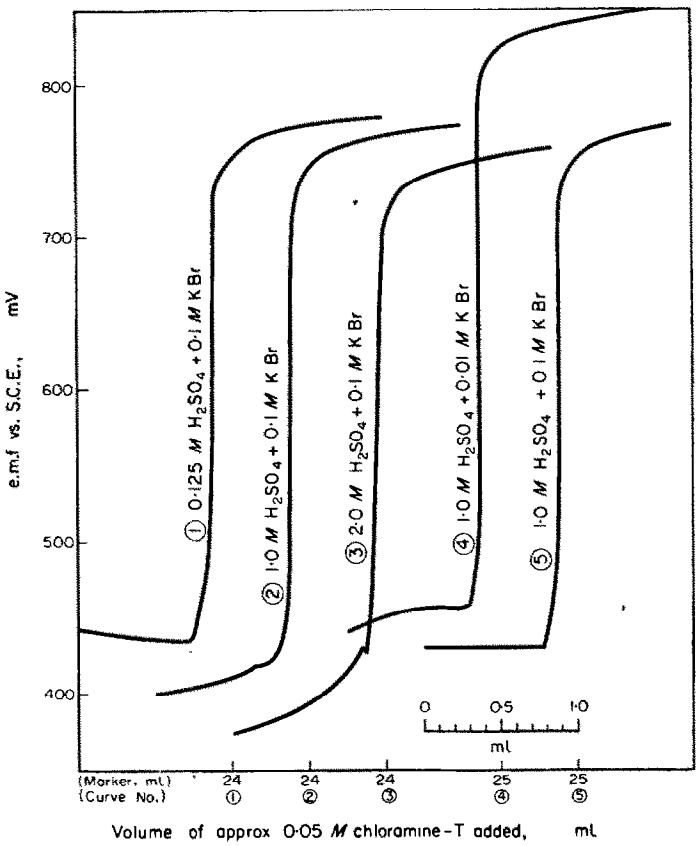


FIG. 4.—Direct titration with approx. $5 \times 10^{-2}M$ chloramine-T of 25-ml aliquots of approx. $5 \times 10^{-2}M$ antimonyl tartrate in sulphuric acid-bromide media at an equivalence point volume of 200 ml.

Since arsenic^{III} can be accurately titrated in either acid under the same conditions,[2] it is evident that the late end-points are caused by the higher potential of the antimony system, with which chloramine-T reacting through the active species bromine is unable to cope, but with which bromate reacting through bromine monochloride[14] can deal

(*b*) *Rosaniline as visual indicator.* Attempted titrations in 0·125, 0·25, 1·0 and. 2·0*M* sulphuric acid in either 0·01 or 0·1*M* bromide were unsuccessful since no sharp end-points were found. The purple colour of the brominated rosaniline appeared gradually somewhere near the calculated equivalence point, but it was impossible to decide to within 0·05 ml the exact location of the end-point.

5. *Reaction in bicarbonate buffer containing iodide*

(*a*) *Starch as visual indicator.* Titrations in two strengths of bicarbonate solution over a range of iodide and tartrate concentrations were conducted using 2 ml of fresh 1% starch solution as indicator added 1 ml before the end-point. Titration proved

impracticable with just the amount of tartrate furnished by the standard antimony solution or with the addition of 0·2 g of tartaric acid, since hydrolysis produced precipitates which reacted very slowly with the iodine formed as the reacting species. With an additional 0·5–1 g of tartaric acid, the results (Table IV) were excellent and highly accurate in 0·2–0·4*M* bicarbonate and 5×10^{-3} to 5×10^{-4}*M* iodide.

(*b*). *Potentiometric titration.* Potentiometric titration under the conditions out-

TABLE IV.—TITRATION OF ANTIMONY^{III} IN BICARBONATE BUFFER CONTAINING IODIDE AND TARTRATE WITH APPROX. 0·05*M* CHLORAMINE-T, USING STARCH AS INDICATOR[b]

Volume of 1*M* $NaHCO_3$ added, *ml*	Tartaric acid added, *g*	Iodide concn., *M*	Measured pH at end-point	End-point, *ml*	Error, %
20	0	5×10^{-3}	—	none	—
20	0·15	5×10^{-3}	—	none	—
20	0·2	5×10^{-3}	7·06	23·81	0
20	0·5	5×10^{-4}	7·10	23·81	0
20	1·0	5×10^{-3}	6·40	23·81	0
20	1·0	5×10^{-3}	—	23·82[a]	+0·04
20	1·0	5×10^{-4}	6·33	23·81	0
40	0	5×10^{-3}	—	none	—
40	0·2	5×10^{-3}	—	none	—
40	0·5	5×10^{-3}	7·28	23·81	0
40	0·5	5×10^{-3}	—	23·82[a]	+0·04
40	0·5	5×10^{-4}	7·28	23·81	0
40	1·0	5×10^{-3}	7·06	23·81	0
40	1·0	5×10^{-3}	—	23·82[a]	+0·04
40	1·0	5×10^{-4}	7·06	23·81	0
40	1·0	5×10^{-4}	—	23·81[a]	0

[a] Potentiometric titration, see Fig. 5.
[b] Calculated equivalence point 23·81 ml.

lined in (a) amply confirmed the accuracy of the method. Four sample curves for various conditions are given in illustration in Fig. 5, and the end-points are included in Table IV. The second inflection in curve 1 corresponds to the oxidation of all the iodide present to iodine.

Titration in amply buffered media with adequate additions of iodide and complexing agent affords an accurate determination of antimony.

CONCLUSIONS

1. Chloramine-T can be used for the accurate determination of antimony^{III} in hydrochloric acid solution in the absence of other halides in the range of acid concentration 1–4*M* by the potentiometric method and 1–3*M* using amaranth as a visual indicator. Tartaric acid up to 6% w/v can be tolerated within these ranges without introducing errors, but positive errors arise with greater quantities of tartaric acid.

2. Amaranth and bordeaux are particularly recommended as indicators for the titration in 2*M* hydrochloric acid. Tartrazine, *p*-ethoxychrysoïdine and methyl orange are also useful, but are subject to certain errors and defects.

3. Addition of bromide to the titration solution affords no advantage. Late end-points arise in the presence of bromide and become later as the bromide concentration increases. The indicator rosaniline gives reasonably correct results, best in 0·5–1·0*M* hydrochloric acid and 0·01*M* bromide. Whilst antimony^{III} can be determined in the presence of bromide, the method is not of sufficient merit to warrant recommendation.

4. Sulphuric acid is an unsuitable medium for the reaction. End-points are obtainable in the presence of bromide but are of poor quality and the results are very high. This state of affairs is not peculiar to the titrant chloramine-T, and is caused in part by the formation of sulphate complexes of antimony.

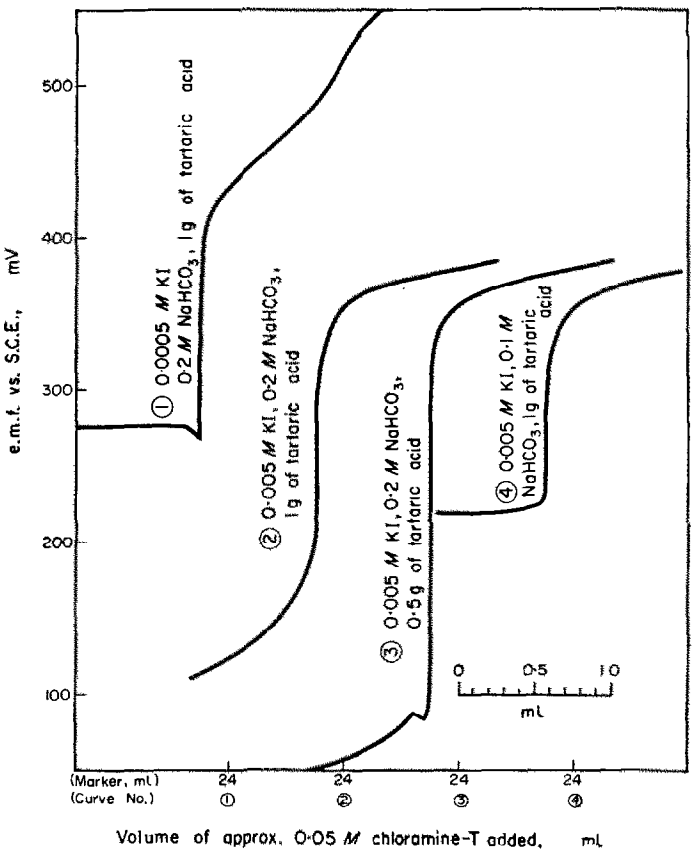


FIG. 5.—Direct titration with approx. $5 \times 10^{-2}M$ chloramine-T of 25-ml aliquots of approx. $5 \times 10^{-2}M$ antimonyl tartrate in bicarbonate buffer containing iodide and tartrate, at an equivalence point volume of 200 ml.

5. Titration with chloramine-T gives highly accurate results in adequately buffered media of pH 6·5–7·5 in the presence of 5×10^{-4} to $5 \times 10^{-3}M$ iodide if sufficient tartrate is added to prevent the formation of a precipitate. At low pH values the reaction is inhibited by the increased oxidation potential of the Sb^{V}/Sb^{III} system, and ceases at higher pH values because of hydrolysis of iodine. Since the primary reaction of chloramine-T with iodide to produce the active oxidising species, iodine, consumes hydrogen ion,[4] care must be taken to provide adequate buffer capacity to prevent the pH running undesirably high.

6. Accurate determination of antimony^{III} with chloramine-T has also been shown[1] to be possible in $3M$ hydrochloric acid with the addition of 2–5 ml of $0{\cdot}1M$ iodine monochloride both potentiometrically and with amaranth as indicator, but the acid concentration is critical.

Zusammenfassung—Ein kritische Untersuchung der Titrationen von Sb(III) mit Chloramin-T wurde durchgeführt. Weite Änderungen in Konzentration von Salz- und Schwefelsäure, sowie der Einfluss von Puffern, in Gegenwart und Abwesenheit von Halidsalzen und Komplexbildnern wurde studiert. Zahlreiche reversible und irreversible Indicatoren wurden ebengalls untersucht. Genaue Resultate werden erhalten in 1–4 m Salzsäure mit potentiometrischer Anzeige und in 1–3 m Salzsäure mit Amaranth als Indicator. Beide Znzeigen erfolgen zu spät in Gegenwart von Bromid und Schwefelsäure, mit oder ohne Halidzusätzen. Einige andere Indicatoren sind in 2 m Salzsäure anwendbar. Titration in ausreichend gepufferter Lösung von pH 6.5–7.5 in Gegenwart von 5×10^{-4}–5×10^{-3} n Jodid geben die besten Resultate. In 3 m Salzsäure werden zufriedenstellende Resultate erhalten, wenn 2–5 ml 0.1 m Jodmonochlorid zugesetzt werden. Potentiometrische Indication und Amaranth arbeiten gut, doch sind die Bedingungen innerhalb eines engen Bereiches einzustellen.

Résumé—Les auteurs ont fait une étude critique du dosage de l'antimoine par la chloramine-T dans un grand domaine de conditions en milieux acide chlorhydrique, acide sulfurique et tamponné, en présence et en l'absence de concentrations variées d'ion halogénure et d'agent complexant, par la méthode potentiométrique. Un grand nombre d'indicateurs réversibles et irréversibles ont aussi été étudiés dans ces conditions. Des dosages précis sont possibles par titrage potentiométrique dans l'acide chlorhydrique 1 à 4*M*, et en utilisant comme indicateur l'amarante dans l'acide chlorhydrique 1 à 3*M*. Divers autres indicateurs sont utilisés dans l'acide chlorhydrique 2 *M*. Les deux méthodes, potentiométrique et avec indicateur visuel, donnent des points équivalents retardés en présence de bromure; et l'acide sulfurique avec et sans addition d'halogénure est un milieu qui ne convient pas. Le titrage dans des milieux convenablement tamponnés de pH 6,5 à 7,5 en présence d'iodure $5 \cdot 10^{-4}$ à $5 \cdot 10^{-3}M$ donne d'excellents résultats et est probablement la meilleure méthode. En milieu acide chlorhydrique 3*M*, avec addition de 2 à 5 ml. de monochlorure d'iode 0,1*M* des résultats satisfaisants sont obtenus en utilisant soit l'amarante, soit la potentiométrie pour déterminer le point équivalent, mais les conditions sont critiques.

REFERENCES

[1] E. Bishop and V. J. Jennings, *Talanta*, 1962, **9**, 581.
[2] *Idem, ibid.*, 1961, **8**, 22.
[3] *Idem, ibid.*, 1961, **8**, 34.
[4] *Idem, ibid.*, 1958, **1**, 197.
[5] F. Rupp, *Pharm. Zentralhalle*, 1925, **66**, 35.
[6] O. Tomicek and B. Suchanla, *Casopis Ceskoslov Lekarnictva*, 1931, **11**, 285, 309.
[7] A. MacMillan and W. Easton, *J. Soc. Chem. Ind.*, 1927, **46**, 472T.
[8] W. Poethke and F. Wolf, *Z. anorg. Chem.*, 1952, **268**, 244.
[9] E. Bishop, unpublished work, 1942–44.
[10] E. Bishop, G. D. Short and J. M. Ottaway, *Analyt. Chim. Acta*, in press.
[11] E. Bishop and V. J. Jennings, *Talanta*, 1961, **8**, 697.
[12] V. J. Jennings, *Titrimetric Analysis with chloramine-T*, Univ. Exon. 1957.
[13] E. Bishop, *Analyt. Chim. Acta*, 1959, **20**, 315.
[14] E. Schulek, K. Burger and J. Laszlovsky, *Talanta*, 1960, **7**, 51.

Talanta, 1962, Vol. 9, pp. 603 to 609. Pergamon Press Ltd. Printed in Northern Ireland

TITRIMETRIC ANALYSIS WITH CHLORAMINE-T–VII*

THE CHLORAMINE-T—HYDRAZINE REACTION

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Summary—The determination with chloramine-T of hydrazine in hydrochloric acid, sulphuric acid and buffer media with and without the addition of halides under a wide variety of conditions has been critically examined both potentiometrically and using a number of visual indicators. Under suitable conditions, analytically useful results are obtainable, but expectations raised by the ease of purification of hydrazine sulphate and the very high accuracy of its determination with other oxidants have not been fulfilled, and chloramine-T cannot be recommended for the accurate determination of hydrazine under any conditions.

THE remarkable promise, at present under investigation, of hydrazine sulphate as a primary standard, and the precision and accuracy of its titrimetric reactions with bromate,[2] iodate,[3,4] and alkalis,[5] suggested that it might afford a valuable alternative to arsenic^{III} in the standardisation of chloramine-T solutions.[6] Arsenious oxide, even after sublimation in oxygen, is slightly hygroscopic, which renders weighing difficult, whereas hydrazine sulphate does not suffer from this disadvantage. Preliminary investigations, however, quickly showed that the reaction in the presence of bromide with chloramine-T could not replace the oxidation of hydrazine by bromate.

Previous work on this reaction is scanty. Hydrazine has been titrated in sodium bicarbonate solution containing "a crystal" of potassium iodide and with starch as indicator;[8] no study of conditions is reported. It has also been titrated potentiometrically in hydrochloric acid solution of unspecified concentration,[9] and in the presence of bromide;[10] no details are given. Titration by the Andrews method has already been critically examined.[11]

Cahn and Powell[12] have studied the mechanism of oxidation of hydrazine in aqueous solution, and report three possible reactions, depending on the nature of the oxidant:

$$N_2H_5^+ = 4\varepsilon + N_2 + 5H^+ \quad (1)$$

$$2N_2H_5^+ = 2\varepsilon + 2NH_4^+ + N_2 + 2H^+ \quad (2)$$

$$2N_2H_5^+ = 4\varepsilon + HN_3 + NH_4^+ + 5H^+ \quad (3)$$

Certain oxidants, notably acidified iodate, give reaction (1) quantitatively, some give reactions (1) and (2) simultaneously, while reaction (3) is rare. In the attempt to oxidise hydrazine with chloramine-T according to reaction (1), should the other reactions occur then less than the amount of chloramine-T calculated for reaction (1) will be consumed. As will be shown, the errors are mostly positive, and in such instances as yield negative errors there is strong evidence that these are caused by slowness of

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reaction. Under favourable conditions, therefore, reaction (1) occurs to the exclusion of the alternatives. At hydrochloric acid concentrations of 1*M* or more, in the absence of other halides, very low and highly erratic results indicate that reaction (2) may be occurring.

EXPERIMENTAL

The preparation and purity of materials, the preparation and standardisation of solutions, and the preparation of reagents, indicators and buffers have been described.[1,6,7,11,13–15]

The methods of conducting visual indicator and potentiometric titrations have also been described.[6,7,13,14] The equivalence point volume of visual indicator titrations was arranged to be 100 ml, that of potentiometric titrations 200 ml, and the concentrations quoted refer to the equivalence point, due allowance for washing being made.

RESULTS AND DISCUSSION

1. *Reaction in chloride media*

Direct titration of hydrazine in hydrochloric acid of concentrations from 2·0 to 0·5*M* using amaranth as indicator gave inaccurate and irreproducible results, as shown in Table I, though it appears that the consumption of oxidant increases with decrease in

TABLE I.—TITRATION OF HYDRAZINE IN HYDROCHLORIC ACID MEDIUM WITH CHLORAMINE-T

Concentration of HCl, *M*	Indication	Titre, *ml*	Error, %
2	Amaranth	20·50	−12·8
2	Amaranth	21·00	−10·7
1	Amaranth	21·50	−8·6
1	Amaranth	21·87	−7·0
0·5	Amaranth	23·89	+1·6
0·5	Amaranth	23·73	+0·9
0·1	Potentiometric	23·83	+1·3

Calculated equivalence point, 23·52 ml.

acid concentration. Titration in hydrochloric acid of concentration greater than 0·5*M* is clearly valueless, while at lower acid concentrations the indicator amaranth merely fades slowly in the absence of bromide and gives no clear end-point. Potentiometric titration (Fig. 1) at an acid concentration of 0·1*M* gave high results, in agreement with amaranth at 0·5*M*. Though the potentials equilibrated rapidly before and after the end-point, the potentials at the end-point required more than 30 min to become steady.

Titration by any means in pure hydrochloric acid medium is totally unsatisfactory, in disagreement with the statement of Singh and Rehmann.[9] It may be noted that bromate gives similarly erratic results in the absence of added bromide.[2]

Reaction at high hydrochloric acid concentrations in the presence of iodine monochloride as a reaction intermediate[11] gives reasonable results, fairly consistent both potentiometrically and with carbon tetrachloride as indicator, but still about 0·1% high, amaranth giving yet higher results. This method has been commended[11] as the most satisfactory with chloramine-T as the titrant.

2. *Reaction in bromide media*

The influence of bromide at an equivalence point concentration of 0·1*M* was investigated both potentiometrically and with visual indicators over a wide range of acid concentrations.

(*a*) *Using rosaniline or amaranth as internal indicators.* With rosaniline, the colour change in 4·0*M* hydrochloric acid was poor and slow, while in 1·0*M* hydrochloric acid the purple colour was faintly visible 0·1 ml before the end-point which was itself early. Acid concentrations of 2 and 3*M* gave sharp end-points, but the reproducibility was

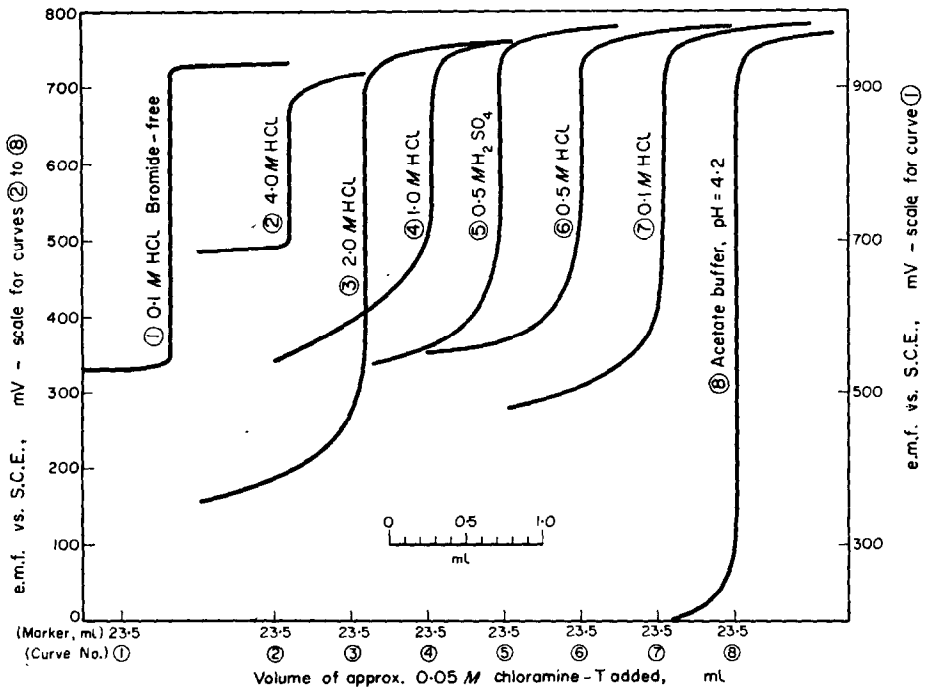


FIG. 1.—Direct titration of 25-ml aliquots of approx. $2·5 \times 10^{-2}M$ hydrazine in media 0·1*M* in bromide (except curve 1) at an equivalence point volume of 200 ml, with approx. $5 \times 10^{-2}M$ chloramine-T.

unsatisfactory. This contrasts sharply with highly accurate results obtainable with bromate under the same conditions. With amaranth, the end-point occurs progressively earlier as the hydrochloric acid concentration falls from 2·0 to 0·5*M*, then becomes later at 0·1*M* and in acetate buffer of pH 4·2. Although the end-points are reasonably sharp, they are not reproducible and vary widely with acid concentration. The results recorded in Table II are individual values given in illustration of the variation observed.

(*b*) *Potentiometric titration.* Titrations conducted under conditions similar to those in (*a*) gave curves shown in Fig. 1. Pre-end-point potentials were unsteady but after the end-point the equilibration was rapid. The shape of the curve follows a form of progression from pH 0 to pH 4·2. Variations in the results (Table II) similar to those with amaranth were observed, but the agreement in values is poor. That the nature of the acid is unimportant is indicated by the resemblance between the curves for 0·5*M* hydrochloric and 0·5*M* sulphuric acids, though the disparity in end-point (0·04 ml) is greater than the experimental error.

TABLE II.—TITRATION[b] OF HYDRAZINE IN MEDIA 0·1*M* IN POTASSIUM BROMIDE WITH CHLORAMINE-T

Conditions at equivalence point	Potentiometric		Amaranth		Rosaniline	
	End-point *ml*	Error %	End-point *ml*	Error %	End-point *ml*	Error %
4·0*M* HCl	23·60	+0·34	—		23·62	+0·43
3·0*M* HCl	—		—		23·58	+0·26
2·0*M* HCl	23·60	+0·34	23·57	+0·21	23·57	+0·21
1·0*M* HCl	23·54	+0·09	23·49	−0·13	23·45	−0·30
0·5*M* HCl	23·51	−0·04	23·42	−0·43	—	
0·5*M* H_2SO_4	23·48	−0·17	—		—	
0·1*M* HCl	23·54	+0·09	23·50	−0·09	—	
Buffer[a] pH 4·2	23·51+	0	23·52	0	—	

[a] Add 25 ml of a solution 0·6*M* in sodium acetate and 1·4*M* in acetic acid for an equivalence point volume of 100 ml.

[b] Calculated equivalence point, 23·52 ml.

The presence of bromide gives a considerable improvement in the results, which are fairly satisfactory at hydrogen ion concentrations of 10^{-4} to 4·0*M* for the potentiometric method, 10^{-4} to 2·0*M* for amaranth, and 2·0–4·0*M* for rosaniline. The results do not in any way compare in precision or accuracy with the bromate method, so chloramine-T cannot be recommended for the accurate determination of hydrazine even in the presence of bromide. The end-points are sharp, and fall within ±0·1 ml of the equivalence point over the range of conditions examined, and occasional results are in quantitative agreement with theory, but the end-points are not reproducible, and there is therefore an uncertainty which enforces the conclusion that the method is not sound.

3. *Reaction in iodide media*

Audrieth and Ogg[16] report that in the titration of hydrazine with iodine solutions, the pH of the titration solution should be maintained between 7 and 7·4. At lower values, the reaction between iodine and hydrazine is quantitative but slow, while at higher values low results occur because of air oxidation of the hydrazine. The present investigation covers a range of pH values and iodide concentrations.

(*a*) *Using starch as an internal indicator.* Addition of 2 ml of 1% starch solution 1 ml before the equivalence point and titration to the first perceptible permanent blue colour gave the results shown in Table III. The results appear to be equally satisfactory or unsatisfactory in all the conditions examined. However, at pH 6·6, the reaction was slow, iodine being liberated prematurely and disappearing gradually. This effect is most marked at the highest iodide concentration. At pH 7·1 the titrations were qualitatively satisfactory and the results were reasonably reproducible though still high, except in $5 \times 10^{-3}M$ iodide when unusually early end-points appeared. At pH 8·3, the end-points became less sharp as the iodide concentration is increased because of the production of a brown colour prior to the iodine blue. The results do not indicate air oxidation of hydrazine.

(*b*) *Potentiometric titration.* An illustrative family of curves is given in Fig. 2 and the results in Table III. In all of the titrations the potentials were unsteady before the

TABLE III.—TITRATION OF HYDRAZINE IN IODIDE MEDIA WITH CHLORAMINE-T

Calculated equivalence point, 23·52 ml.

Buffer	Iodine concn, *M*	Potentiometric End-point *ml*	Potentiometric Error %	Starch End-point *ml*	Starch Error %
20 ml of I	0·005	23·60	+0·34	23·51	−0·04
	0·025	23·60	+0·34	23·57	+0·21
	0·05	23·57	+0·21	23·57	+0·21
15 ml of II	0·005	23·49	−0·13	23·40	−0·51
	0·025	23·57	+0·21	23·57	+0·21
	0·05	—		23·57	+0·21
	0·10	23·58	+0·26	23·57	+0·21
20 ml of III	0·005	23·60	+0·34	23·56	+0·17
	0·025	23·60	+0·34	23·58	+0·26
	0·05	23·60	+0·34	23·61	+0·38

Buffer solutions:

I. Solution 0·1*M* in potassium dihydrogen phosphate and 0·233*M* in disodium hydrogen phosphate; measured pH at equivalence point, 6·6 for starch, 6·7 for potentiometric titration.

II. Solution 0·0167*M* in potassium dihydrogen phosphate and 0·317*M* in disodium hydrogen phosphate; measured pH at equivalence point 7·1 for starch, 7·2 for potentiometric titration.

III. 1*M* sodium bicarbonate; measured pH at equivalence point, 8·3, in both indicator and potentiometric titrations.

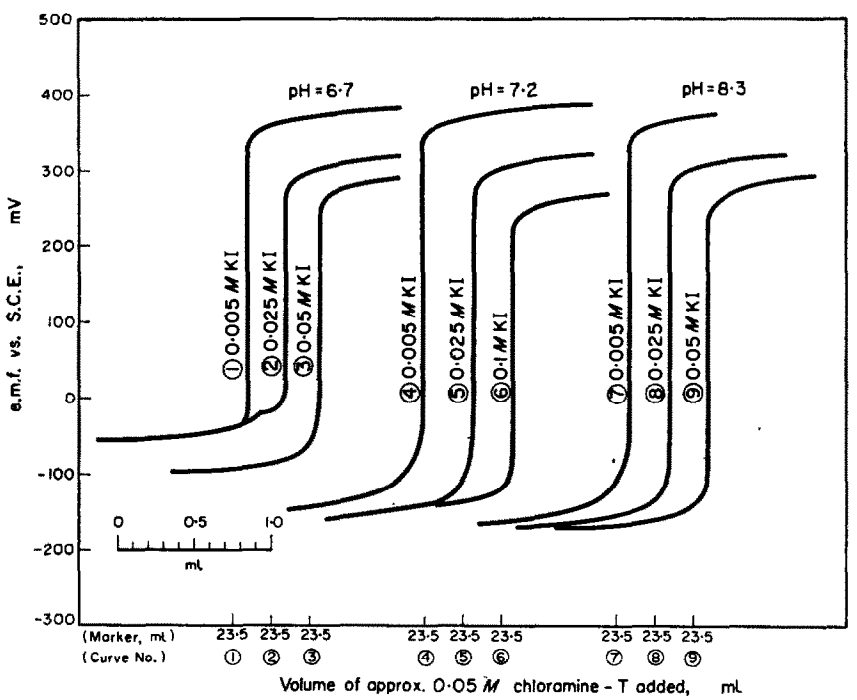


FIG. 2.—Direct titration of 25-ml aliquots of approx. 2·5 × 10^{-2}*M* hydrazine in various buffer media in the presence of iodide, with approx. 5 × 10^{-2}*M* chloramine-T.

end-point, but equilibrated rapidly after the end-point, and the yellow iodine colour became visible 0·02 ml after the recorded end-point. The results agree fairly well with those of the visual indicator titrations, with a tendency to be somewhat later. There is again no evidence for air oxidation at high pH values.

The conditions for titration of hydrazine in an iodide medium are rather critical, the most favourable being a pH of 7·1, in agreement with Audrieth and Ogg,[16] and an iodide concentration of 0·025–0·05*M*. This does not entirely accord with the claims of Komarovsky *et al.*[8] The results are in fair agreement with the preferred method of titration in presence of iodine monochloride at high hydrochloric acid concentrations.[11]

CONCLUSIONS

Expectations of the reaction between chloramine-T and hydrazine have not been fulfilled. Hydrazine can be determined by titration with chloramine-T in media containing bromide, iodide or iodine monochloride under the conditions specified, with an accuracy suitable for routine work, but none of the methods yields results of a calibre suitable for accurate work or for standardising chloramine-T solutions. Chloramine-T cannot, therefore, be substituted for bromate in this determination. The same exclusion applies in the determination of hydroxylamine,[7] for which no satisfactory results are obtainable, and in the determination of antimony,[1,7] and of thallium.[7,17] The reason for this is obscure, because in the presence of bromide both oxidants react through the same active species, bromine.

High results for hydrazine are of frequent occurence under many conditions, and would seem to exclude the reactions (2) and (3) in these conditions. It is possible that reaction (4) occurs to a small extent.

$$N_2H_5^+ + H_2O = N_2O + 7H^+ + 6\varepsilon \qquad (4)$$

No direct indentification of nitrous oxide has been made in this case, but it has been observed in the products of oxidation of hydrazine by vanadate.[18]

Chloramine-T cannot be recommended for the accurate determination of hydrazine under any conditions.

Zusammenfassung—Die Titration von Hydrazin mit Chloramin T in salzsaurem, schwefelsaurem und gepuffertem Medium, mit und ohne Halidzusätzen wurden studiert. Endpunktanzeige war potentiometrisch und visuell mit verschiedenen Indikatoren. Unter geeigneten Bedingungen können verwendbare Resultate erhalten werden. Da jedoch zahlreiche, ausgezeichnete Methode auf anderer Basis existieren wird diese Titration nicht empfohlen.

Résumé—Les auteurs ont étudié d'un point de vue critique le dosage de l'hydrazine par la chloramine T en milieux acide chlorhydrique, acide sulfurique et tamponné, avec et sans addition d'halogénures en faisant varier un grand nombre de conditions; la potentiométrie et un certain nombre d'indicateurs visuels ont été utilisés pour déterminer le point équivalent. Dans des conditions convenables, des résultats utilisables au point de vue analytique ont été obtenus, mais les prévisions attendues à cause de la facilité de purification du sulfate d'hydrazine et de la très grande précision de son dosage par d'autres oxydants n'ont pas été réalisées; la chloramine T ne peut donc pas être recommandée pour le dosage précis de l'hydrazine dans n'importe quelle condition.

REFERENCES

[1] E. Bishop and V. J. Jennings, *Talanta*, 1962, **9**, 593.
[2] E. Bishop, *Analyst*, 1960, **85**, 422.
[3] G. F. Smith and C. S. Wilcox, *Ind. Eng. Chem. Analyt.*, 1942, **14**, 49.
[4] B. Singh and I. Ilani, *J. Indian Chem. Soc.*, 1937, **14**, 376.

[5] K. Komarek, *Chemie* (Prague) 1948, **3,** 102; A. J. Nutten, *Metallurgia*, 1949, **41,** 111.
[6] E. Bishop and V. J. Jennings, *Talanta*, 1958, **1,** 197.
[7] V. J. Jennings, *Titrimetric Analysis with Chloramine-T*, Univ. Exon., 1957.
[8] A. S. Komarovsky, W. F. Filanova and I. M. Korenman, *Z. analyt. Chem.*, 1934, **96,** 321.
[9] B. Singh and A. Rehmann, *J. Indian Chem. Soc.*, 1940, **17,** 167.
[10] B. Samek, *Chem. Zentr.*, 1942, **1,** 517; *Chem. Abs.*, 1942, **37,** 2683.
[11] E. Bishop and V. J. Jennings, *Talanta*, 1962, **9.**
[12] J. W. Cahn and R. E. Powell, *J. Amer. Chem. Soc.*, 1954, **76,** 2568.
[13] E. Bishop and V. J. Jennings, *Talanta*, 1961, **8,** 22.
[14] *Idem, ibid.*, 1961, **8,** 34.
[15] *Idem, ibid.*, 1961, **8,** 697.
[16] L. E. Audrieth and B. A. Ogg, *The Chemistry of Hydrazine.* John Wiley and Son, Inc, New York, 1951. p. 153.
[17] E. Bishop and V. J. Jennings, paper to be submitted.
[18] E. Bishop and A. Fagan, unpublished work, 1946.

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APPLICATIONS OF INFRARED SPECTROSCOPY—VII*

THE BEHAVIOUR OF THIOALKYL COMPOUNDS UNDER ZEISEL REACTION CONDITIONS.

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(*Received* 13 *February* 1962. *Accepted* 28 *February* 1962)

Summary—Vapour-phase infrared spectroscopy has been used to study the behaviour of a wide range of thioalkyl compounds when refluxed with constant-boiling hydriodic acid. A very wide range of reactivity has been observed. Unusually labile compounds exist which react quantitatively in less than 3 hr; the kinetics of the decomposition of such compounds must be investigated individually, since over-production of methyl iodide can occur. Many thiomethyl compounds, however, do not yield methyl iodide, and others react very slowly, giving variable non-quantitative yields of methyl iodide after reflux for 16-20 hr. It is therefore concluded that the mere extension of Zeisel reaction conditions for prolonged reflux periods does not usefully provide a general method for the functional group analysis of thioalkyl compounds.

THIOALKYL compounds, which are of current interest in sugar chemistry,[1] yeast metabolism,[2] choline-esterase inhibition,[3] and the chemistry of food-stuffs,[4] have received considerable attention in recent years.

A modified Zeisel reaction[5] has long been used in protein studies to determine the thiomethyl group in methionine. Kassel and Brand[6] suggested improvements to Baernstein's method,[5] and the method of Kuhn, Birkofer and Quackenbush[7] was modified[8] so that both alkoxyl and thiomethyl groups could be determined.

Much is known of the chemistry of thioethers.[9,10,11] The analytical methods applicable to mercapto groups, disulphides and sulphides (thioethers) have been reviewed,[12,13,14,15] and special methods continue to be described,[16,17,18] particularly for biological materials. Many thioethers are cleaved at pH 8–10 by silver or mercury salts;[10] fission of the carbon-sulphur bond has been more extensively studied in alkaline solution[19] than in acids.[20] In general, thioethers and thiolesters react much more slowly in aqueous acids than do their oxygen analogues,[20,21] although the ease of cleavage of carbon-sulphur bonds is influenced by the presence of substitution[22] and β-unsaturation[11] in the molecule.

Early investigators[23,24] reported applications of a modified Zeisel reaction to aromatic thiomethyl compounds, in which a longer reaction period (which was not specified) was required (*cf.* ref. 25). It has been observed,[26] however, that some compounds do not give quantitative results; *S*-methylthiamin[27] gives only 33% of the theoretical yield of methyl iodide. It is apparent that early investigators were involved in considerable experimental difficulties,[23,24] particularly when gravimetric methods were used. A wide range of thioethers and thiolesters has therefore been studied by the infrared method[28] in an attempt to clarify some of the reported anomalies.

* Part VI: D. M. W. Anderson, *Talanta*, 1961, **8**, 832

EXPERIMENTAL

Apparatus

The apparatus has been described elsewhere,[28] together with the technique for trapping volatile reaction products and the infrared method for their subsequent identification and estimation.

Compounds

The majority of compounds investigated were reagent-grade commercial samples which conformed, after recrystallisation or distillation where necessary, to literature description. The other compounds investigated were research specimens (kindly provided by Dr. D. Leaver of this department and by Dyestuffs Division, Messrs. I.C.I. Ltd.) for which satisfactory elemental analyses existed or were obtained (Messrs. Weiler and Strauss, Oxford, England).

Procedure

Samples of the compounds listed in Table I were refluxed, for the periods indicated, with hydriodic acid (6 ml of constant-boiling azeotrope, pre-conditioned[28]) using cylinder nitrogen ("N.O.F." grade) as flow-gas (6-8 ml per min). Sample weights giving 1-4 mg of methyl iodide were normally taken: larger samples were used to permit the identification of minor reaction products. The compounds were dissolved with care in molten phenol[28] before addition to the reaction-flask; a recent report[29] has confirmed the effectiveness of this technique. The mixture of volatile products was collected, after passage through Anhydrone, in a trap immersed in liquid nitrogen. The components of each mixture were subsequently identified by vapour-phase infrared spectroscopy by reference to spectra obtained from authentic compounds. None of the mixtures was sufficiently complex for prior separation of the components by G. L. C. to be necessary, and the presence of other components did not interfere with the determination of methyl iodide.

RESULTS

All compounds containing sulphur produce some hydrogen sulphide on reflux with hydriodic acid; only volatile products other than hydrogen sulphide are reported below.

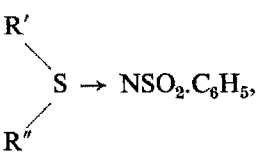
1. *Compounds giving no reaction*

The following thiolesters and thioethers gave no volatile products under Zeisel reaction conditions for reflux periods of 18 hr: methylchlorothiolformate, ethylchlorothiolformate, methyl phenyl sulphide (thioanisole), methyl-α-naphthyl sulphide, 2-thiomethyl-1,4-naphthoquinone, 3-methyl-2-thiomethyl-1,4-naphthoquinone.

The following compounds were partially volatilised, without reaction, from the reaction-flask: methyl and ethyl mercaptan, dimethyl and diethyl sulphide, dimethyl and diethyl disulphide.

2. *Compounds which react but do not yield alkyl iodide*

Dimethyl sulphide was produced from dimethylsulphoxide (fast) and from dimethylsulphone (slow), whilst compounds of the type



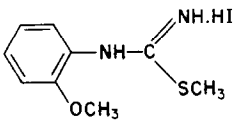
where R′, R″ = *methyl* or *ethyl*, liberated the corresponding dialkyl sulphide. Phenacyl methyl trithiocarbonate gave carbon dioxide, carbon monoxide, and methyl mercaptan.

3. *Compounds which react, yielding alkyl iodide and other volatile products*

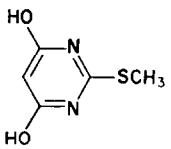
Thiodiglycol and compounds containing the $—S(CH_2.CH_2OH)_2$ grouping gave

ethyl iodide + ethylene in 1-2 hr. Such compounds therefore react similarly to glycols and glycol ethers.[30]

Thiocyanato-methane gave 1 mole of methyl iodide in 2·5 hr, together with some thiocyanogen. The same product was also given by (I) which gives 1 mole of methyl iodide (from the alkoxyl group) in 0·5 hr; the total yield of methyl iodide reached 2 moles after reflux for 20 hr.



(I)



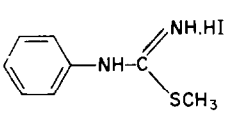
(II)

4. *Compounds which yield only methyl iodide*

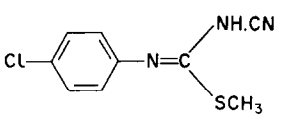
Table I lists the kinetic results obtained.

TABLE I.—THE RATE OF PRODUCTION OF METHYL IODIDE FROM SOME THIOMETHYL COMPOUNDS

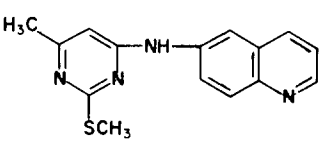
Compound	Moles of methyl iodide produced per mole of compound
2-(Methylthio)benzo-thiazole	0·44 (0·5 hr); 0·76 (1 hr); 0·87 (2 hr); 0·99 (3 hr); 1·12 (4 hr)
S-Methylthiouronium sulphate	0·35 (2 hr); 0·60 (3 hr); 0·98 (4 hr); 1·05 (4.5 hr)
II	0·30 (1 hr); 0·45 (2 hr); 0·55 (2·5 hr); 0·76 (3-4 hr, const.)
III	0·50 (16 hr); 0·52 (20 hr)
IV	0·49 (20 hr)
V	0·25 (12 hr); 0·30 (18 hr)
Methyl-*p*-tolyl sulphide	0·25 (16 hr)
Methyl-*p*-nitrophenyl sulphide	0·15 (17 hr)
Methionine	0·86 (0·5 hr); 0·96 (1 hr); 0·99 (2 hr); 1·15 (2·5 hr); 1·25 (3 hr)
N-Acetyl-DL-methionine	0·86 (1 hr); 1·00 (1·5 hr); 1·22 (2 hr)
Glycyl-DL-methionine	0·1 (15 hr)
S-Methyl-D(+) cysteine	0·15 (2 hr); 0·36 (4 hr); 0·60 (8 hr); 0·70 (16 hr); 0·76 (22-40 hr, const.)
S-Methylglutathione	0·14 (2 hr); 0·46 (8 hr); 0·57 (12 hr); 0·66 (18 hr); 0·75 (22-40 hr, const.)



(III)



(IV)



(V)

5. *Investigation of amino-acids*

Table I shows the rate of production of methyl iodide from methionine and S-methyl derivatives of amino acids. In connection with the possible over-production

of methyl iodide, it was observed that Baernstein had found[31] all samples of leucine to give small amounts of methyl iodide. Whilst Baernstein considered that this indicated the presence of methionine, the methyl iodide could have arisen from general decomposition of the amino-acid molecules. Whilst one sample of L-leucine (shown by paper chromatography to contain some methionine) did give approximately 0·1 mole of methyl iodide, no methyl iodide was given by two different commercial samples of DL-leucine which gave only one spot when examined by paper chromatography. Similarly no methyl iodide was evolved from the following: cystine, homocystine, djenkolic acid, glutathione (reduced), taurine, glycine, alanine, DL-α-amino-n-butyric acid, DL-α-amino-iso-butyric acid, DL-β-amino-iso-butyric acid, L-valine, DL-valine, DL-nor-valine, DL-nor-leucine, DL-iso-leucine.

DISCUSSION

The results quoted show that, under the conditions of the Zeisel alkoxyl determination, the behaviour of thioalkyl groups is extremely variable. It would be misleading to suggest that the determination of *S*-methyl groups generally follows the procedure for *O*-methyl groups, even if the time of reaction be extended by several hours (*cf.* ref. 25 and 32). Indeed, as might be expected from the known stability of the sulphur-carbon bond,[10,11,20,21] the few labile compounds which do give quantitative yields of methyl iodide can be regarded as exceptions to the general rule; those compounds which react rapidly must be considered as possible sources of anomalous alkoxyl determinations. No generalisations regarding reaction conditions or reflux period required can be made; obviously, the kinetics of decomposition of each thiomethyl compound must be investigated individually (*cf.* ref. 33).

The observed rate of formation of methyl iodide from methionine agrees with that reported by previous workers,[5,6] who observed[6] that small differences in reaction rate can be attributed to variations in the design of apparatus. Baernstein's earliest procedure[5] (1932) recommended a reaction period of 15 hr, but this was later (1934) amended to 3 hr. Our results show the possibility (which does not appear to have been appreciated previously) of over-production of methyl iodide from those thiomethyl compounds which are sufficiently labile to react in short periods.

Theoretical reasons for the failure of aqueous halogen acids to cleave carbon-sulphur bonds as effectively as carbon-oxygen bonds have been discussed (*cf.* refs. 11, p. 36, and 21, p. 677). The very wide range of reactivities observed in thioethers is not unique: a remarkable range of reactivity is also to be found in their oxygen analogues.[34] It is of interest that compound II is not particularly labile, whereas methoxy compounds of this type were found[34] to be unusually reactive in acid solution.

The behaviour of thiomethyl compounds in Herzig and Meyer's pyrolytic procedure[35] for alkimide groups has not been studied. Experiments were made, however, with acid more concentrated (67% HI, sp. gr. 1·94) than the constant-boiling azeotrope (55% HI, sp. gr. 1·70). In agreement with previous reports,[23] the more concentrated acid did not cause appreciably faster liberation of methyl iodide. The addition of large amounts of phenol, propionic anhydride, or mercuric chloride to the reaction mixture[23,24] (*cf.* ref. 11, p. 39) did not influence the kinetic results.

Acknowledgements—We thank Dr. D. Leaver and Messrs. I.C.I. (Dyestuffs Division) Ltd., for providing samples, and the P.C.S.I.R., Karachi, for granting study leave to S. S. H. Z.

Zusammenfassung—Infrarotspectroskopie in der Gasphase wurde angewandt um das Verhalten von Thioalkylverbindungen zu studieren, wenn sie unter Rückfluss mit konstant siedender Jodwasserstoffsäure behandelt werden. Ungewöhnlich labile Komponenten existieren, welche weniger als 3 Stunden zur quantitativen reaktion benötigen. Die Kinetik der Zersetzung solcher Komponenten muss individuell studiert werden, da Überproduktion von Methyljodid auftreten kann. Viele Verbindungen jedoch geben kein Methyljodid, ander reagieren sehr langsam, sodass die Ausbeute selbst nach 16–20 Stunden nicht quantitativ ist. Es wird daher geschlossen, dass die blosse zeitliche Ausdehnung der Zeiselmethode keine allgemeine Methode zur Analyse funktioneller Gruppen in Thioalkylverbindungen ergeben kann.

Résumé—Les auteurs ont utilisé la spectroscopie infra-rouge en phase vapeur pour l'étude du comportement d'un grand nombre de composés thioalcoylés chauffés au reflux avec de l'acide iodhydrique bouillant constamment. Ils ont observé un domaine de réactivité très large. Il existe des composés inhabituellement labiles qui réagissent quantitativement en moins de trois heures; la cinétique de la décomposition de tels corps doit être étudiée individuellement, car il peut y avoir surproduction d'iodure de méthyle. Cependant, de nombreux composés thiométhylés ne donnent pas d'iodure de méthyle et d'autres réagissent très lentement en donnant des rendements variables non quantitatifs en iodure de méthyle après reflux pendant 16–20 heures. On peut donc conclure que le simple développement des conditions de la réaction de Zeisel pour des périodes de reflux prolongées n'apporte pas de méthode générale d'analyse du groupement fonctionnel des composés thioalcoylés.

REFERENCES

[1] M. L. Wolfrom, W. Von Bebenburg and A. Thompson, *J. Org. Ch m.*, 1961, **26**, 4151.
[2] G. A. Maw, *Proc. Biochem. Soc.*, 1960, **80**, 28P.
[3] R. I. Volkova, N. N. Godovikov *et al.*, *Voprosy Med. Khim.*, 1961, **7**, 250.
[4] T. Hasselstrom, R. C. Clapp, L. T. Mann and L. Long, *J. Org. Chem.*, 1961, **26**, 3026.
[5] H. D. Baernstein, *J. Biol. Chem.*, 1932, **97**, 663; 1934, **106**, 451.
[6] B. Kassel and E. Brand, *ibid.*, 1938, **125**, 145.
[7] R. Kuhn, L. Birkofer and F. W. Quackenbush, *Ber.*, 1939, **72**, 407.
[8] A. Holasek, H. Lieb and W. Merz, *Mikrochim. Acta*, 1956, 1216.
[9] E. E. Reid, *Organic Chemistry of Bivalent Sulphur*. Chemical Pub. Co., Inc., New York.
[10] R. Cecil and J. R. McPhee, *Advances in Protein Chemistry*, 1959, **14**, 225.
[11] D. S. Tarbell and D. P. Harnish, *Chem. Revs.*, 1951, **49**, 1.
[12] H. Roth, *Mikrochim. Acta*, 1958, 766.
[13] W. Schöniger, *Chimia*, 1959, 220.
[14] S. Dal Nogare, *Organic Analysis*. Interscience Pub. Inc., New York, Vol. I, p. 329 1953.
[15] A. Steyermark, *Quantitative Organic Microanalysis*. Academic Press Inc., New York, 1961.
[16] I. M. Kolthoff and J. Eisenstädter, *Analyt. Chim. Acta*, 1961, **24**, 83, 280.
[17] T. Goa, *Acta Chem. Scand.*, 1961, **15**, 853.
[18] J. C. Fletcher and A. Robson, *Proc. Biochem. Soc.*, 1961, **80**, 37P.
[19] Y. Iskander and R. Tewfik, *J. Chem. Soc.*, 1961, 223, 2402.
[20] D. P. Harnish and D. S. Tarbell, *J. Amer. Chem. Soc.*, 1948, **70**, 4123.
[21] R. L. Burwell, *Chem. Revs.*, 1954, **54**, 677.
[22] J. Gierer and B. Alfredson, *Chem. Ber.*, 1957, **90**, 1240.
[23] J. Pollak and A. Spitzer, *Monatsh.*, 1922, **43**, 113.
[24] G. Sachs and M. Ott, *ibid.*, 1926, **47**, 415.
[25] A. Elek, *Organic Analysis*, Vol. I, p. 92.
[26] F. Arndt, L. Loewe and M. Ozansoy, *Ber.*, 1939, **72**, 1860.
[27] E. P. Dikella and D. J. Hennessy, *J. Org. Chem.*, 1961, **26**, 2017.
[28] D. M. W. Anderson and J. L. Duncan, *Talanta*, 1960, **7**, 70.
[29] D. L. Miller, E. P. Samsel and J. G. Cobler, *Analyt. Chem.*, 1961, **33**, 677.
[30] P. W. Morgan, *Ind. Eng. Chem., Analyt.*, 1946, **18**, 500.
[31] H. D. Baernstein, *J. Biol. Chem.*, 1936, **115**, 25, 33.
[32] R. H. Cundiff and P. C. Markunas, *Analyt. Chem.*, 1961, **33**, 1028.
[33] F. G. Arndt, *Organic Analysis*, Vol. I, p. 197.
[34] D. M. W. Anderson and J. L. Duncan, *Talanta*, 1962, in press.
[35] J. Herzig and H. Meyer, *Ber.*, 1894, **27**, 319.

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SHORT COMMUNICATIONS

Isotopic-dilution analysis by solvent extraction—IV: *Selective determination of traces of copper with dithizone

(*Received* 6 *February* 1962. *Accepted* 5 *March* 1962)

INTRODUCTION

IN our first communication[1] the theoretical foundation was given for the determination of trace amounts of metals by means of isotopic-dilution analysis by solvent extraction; and in the following papers[2,3] the procedures for highly selective and sensitive determination of zinc and mercury were developed. In the present work, the possibility of using this method for determination of traces of copper has been confirmed. From equilibrium constants of extraction of metal dithizonates[1] it can be seen that in the determination of copper an excess of the following metals will interfere: palladium, mercury, platinum, silver, bismuth and gold. In presence of iodide, which forms very stable complexes with mercury, silver and bismuth,[4] interference from only palladium, platinum and gold may be expected.

EXPERIMENTAL

Apparatus

Scintillation counter with NaI-Tl crystal.

Geiger-Müller end-window counter.

pH-meter: Radiometer TTTl (Copenhagen).

Mechanical shaker.

Glass test-tubes with ground stopper, volume 25 ml.

Reagents

Distilled water: Twice distilled, further purified by passage through a column of ion-exchanger; used for dissolving all reagents.

Carbon tetrachloride: A.R. twice distilled.

Dithizone: A.R.

Buffer solution: Dissolve 15 g of potassium iodide, A.R., 13 g of ammonium acetate, A.R., in 100 ml of water and add glacial acetic acid, A.R., to attain a pH-value of $4{\cdot}8 \pm 0{\cdot}2$. This solution was purified before each experiment by dithizone extraction.

Radio-copper solution (^{64}Cu, $T_{\frac{1}{2}} = 12{\cdot}8$ h): Dissolve copper sulphate (initial specific activity 500 mC/g of copper) in acidified water and dilute to the required concentration.

Non-active copper solution: Dissolve copper sulphate in acidified water and dilute to the required concentration.

Procedure

Add to 10 ml of the test solution of non-active copper (of the order of magnitude of 10^{-7} to 10^{-10} g of copper/ml) which contains a great excess of other metals, a suitable amount of radio-copper, y. The most accurate results are obtained if the amounts of nonactive and active copper are approximately the same. After addition of 1 ml of buffer solution, the pH of the test solution must be 4.8 ± 0.2. If the original solution is too acid, decrease its acidity by addition of a further amount of buffer solution. Extract the solution prepared in this way with about 1 ml of dithizone solution in carbon tetrachloride of suitable concentration (the concentration of dithizone must be always less than the amount which corresponds to the stoicheiometric ratio of copper present). After shaking 10 min, separate the organic phase and measure the activity of 0·6 ml of the solution by a

* Part III: See reference 3.

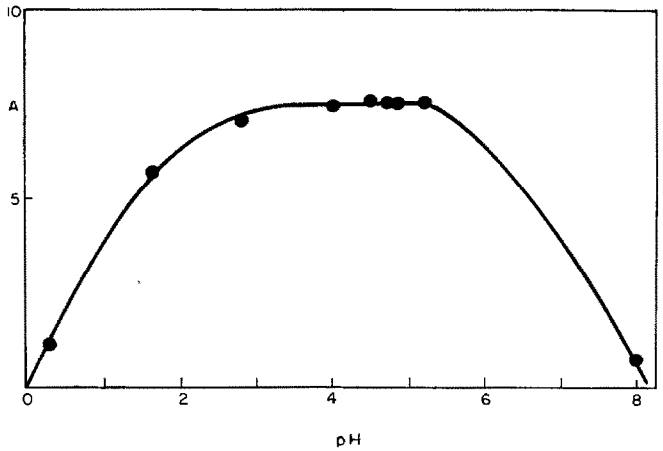


FIG. 1

√—Influence of pH on activity of extract (10^3 cpm.)

TABLE 1.—EXTRACTION OF COPPER BY DITHIZONE.
($1{\cdot}27 \times 10^{-7} - 2{\cdot}4 \times 10^{-10}$ μg of Cu/ml)[a]

Copper taken, μg (x)	Active copper added, μg (y)	Activity of extracts[b] (A_1)	Activity of extracts[b] (A_2)	Copper found, μg (x)	Deviation, μg	Other metals present, μg
1·271	1·083	15,878	7,608	1·117	−0·094	100 μg Zn, Co, Ni, Cd
		15,878	7,410	1·238	−0·033	100 μg Pb, In, Tl
		15,878	7,502	1·209	−0·062	—
		8,015	3,635	1·305	+0·034	100 μg Hg, Ag, Bi
		8,015	3,675	1·279	+0·008	100 μg Zn, Co, Ni, Cd
		8,015	3,687	1·271	0·000	100 μg Pb, In, Tl
		8,015	3,627	1·310	+0·039	—
0·2542	0·2166	4,054	1,824	0·2647	+0·0105	10 μg Hg, Ag, Bi
		4,054	1,860	0·2400	−0·0142	—
0·2654	0·2780	2,548	1,322	0·2578	−0·0076	10 μg Hg, Ag, Bi
		2,548	1,291	0·2707	+0·0153	10 μg Zn, Co, Ni, Cd
		2,548	1,330	0·2546	−0·0108	10 μg Pb, In, Tl
		2,548	1,290	0·2711	+0·0057	10 μg Mn, Sn, Fe
		2,548	1,303	0·2656	+0·0002	—
0·0237	0·0201	1,060	513	0·0213	−0·0024	1 μg Hg, Ag, Bi
		1,060	458	0·0263	+0·0026	1 μg Zn, Co, Ni, Cd
		1,060	495	0·0228	−0·0009	1 μg Pb, In, Tl
		1,060	450	0·0269	+0·0032	1 μg Mn, Sn, Fe
		1,060	488	0·0235	−0·0002	—
		782	367	0·0228	−0·0009	1 μg Hg, Ag, Bi
		782	376	0·0217	−0·0020	1 μg Zn, Ni, Co, Cd
		782	387	0·0205	−0·0032	1 μg Pb, In, Tl
		782	388	0·0204	−0·0033	1 μg Mn, Sn, Fe
		782	360	0·0237	0·0000	—
0·0024	0·0201	1,060	940	0·0022	−0·0002	—
		782	738	0·0021	−0·0003	—

[a] Volume of solution analysed in all experiments listed in Table I was 10 ml.
[b] In the range $1{\cdot}3 \times 10^{-7}$ g of Cu/ml, concentration of dithizone was $2 \times 10^{-5}M$
$2{\cdot}6 \times 10^{-8}$ g of Cu/ml, concentration of dithizone was $5 \times 10^{-6}M$
$2{\cdot}4 \times 10^{-9}$ g of Cu/ml, and $2{\cdot}4 \times 10^{-10}$ Cu/ml, concentration of dithizone was $5 \times 10^{-7}M$

All activities (cpm) listed in Table I are mean values for 4 or 6 measurements.

scintillation counter (for high activity samples) or by a Geiger-Müller counter (for small activity samples). This activity is A_2. At the same time, treat the solution which contains only radio-copper and 1 ml of buffer solution in exactly the same way. Measure the activity of 0·6 ml of the organic phase in the same way (activity A_1).

The amount of non-active copper (x) is calculated from the equation

$$x = y \cdot \left(\frac{A_1}{A_2} - 1\right).$$

RESULTS AND DISCUSSION

The influence of pH on the extraction of copper by a $2 \times 10^{-5}M$ solution of dithizone in carbon tetrachloride is shown in Fig. 1. The volume of the aqueous phase was ten times larger than the volume of the organic phase. Under these conditions, at pH 4·0 to 5·2 the maximum of copper is extracted, which is in agreement with the predicted value.[1] (For the concentration used, the maximum extraction is in the range pH 3·5–5·0.)

In Table I the results of determinations carried out by the procedure described are given. In this determination even a large excess of metals forming extractable complexes with dithizone (mercury, silver, bismuth, zinc, cobalt, nickel, cadmium, lead, indium, thallium, manganese, tin and iron) does not interfere.

This method has been used for the determination of copper in pure water and in urea.

The method is very simple and rapid. A single extraction of copper from a solution containing an excess of interfering metals is appreciably simplier than the conventional colorimetric determination of copper by dithizone. Comparison of our results with values from the literature[5] indicates that the determination of copper by this method is more sensitive (maximum sensitivities of the methods mentioned are given in brackets) than determination by flame photometry (0·1 μg/ml), by the graphite DC arc (0·2 μg/ml), colorimetrically (0·03 μg/ml) or by activation analysis (0·04 μg/ml—5 . 10^{11} neutron/cm^2 sec; 0·002 μg/ml—10^{13} neutron/cm^2 sec).

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Summary—Copper is determined by a single extraction in the form of a complex with dithizone in amounts of 10^{-7} to 10^{-10} g/ml. Even a large excess of metals which form extractable complexes with dithizone do not interfere in the analysis. The method is very simple and rapid, consisting of a single extraction of the solution to be analysed, and measurement of the activity of the extract. The procedure is more sensitive than other methods of determining copper.

Zusammenfassung—Kupfer kann nach einer einzigen Ausschüttellung mit Dithizon in Mengen von 10^{-7}–10^{-10} g/ml bestimmt werden. Die Analyse wird selbst von grossen Mengen anderer Ionen, die mit Dithizon extrahierbar sind, nicht gestört. Die Activität des Extractes wird gemessen. Die Methode ist weit empfindlicher als andere Methoden zur Bestimmung von Kupfer.

Résumé—Le cuivre a été dosé par simple extraction sous forme d'un complexe avec la dithizone pour des quantités de 10^{-7} à 10^{-10} g/ml. Dans l'analyse, même un grand excès de metaux, qui forment avec la dithizone des complexes extractibles, ne gêne pas. La méthode est très simple et rapide, car elle consiste en une extraction de la solution à analyser et en la mesure de l'activité du composé extrait. La méthode mise au point est beaucoup plus sensible que les autres méthodes de dosage du cuivre.

REFERENCES

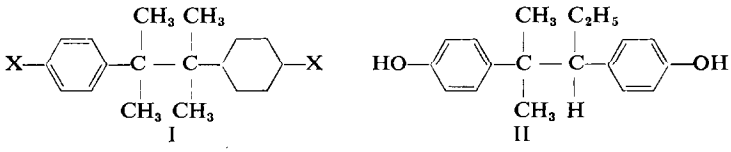
[1] J. Růžička and J. Starý, *Talanta*, 1961, **8**, 228.
[2] J. Starý and J. Růžička, *ibid.*, 1961, **8**, 296.
[3] J. Růžička and J. Starý, *ibid.*, 1961, **8**, 535.
[4] J. Bjerrum, G. Schwarzenbach and L. G. Sillen, *Stability Constants*, Part II The Chemical Society, London, 1958, 33.
[5] J. H. Yoe and J. R. Koch, *Trace Analysis*. New York, 1957, p. 626.

Applications of infrared spectroscopy—VIII*: Investigation of a reported anomalous Zeisel alkoxyl reaction

(*Received* 23 *February* 1962. *Accepted* 28 *February* 1962)

SEVERAL examples of molecules which react anomalously in the Zeisel alkoxyl reaction have been reported,[1,2,3] and solvent retention is known[4,5,6] to be a potential source of error in alkoxyl determinations.

Huang and Morsingh[7] reported that 2,3-dimethyl-2,3-diphenylbutane (I, X = H) and certain of



its derivatives (I, X = OH, NO_2) reacted anomalously in the Zeisel reaction, giving an apparent methoxyl content of 3·3%. Such a result appeared surprising; when it was observed that the experimental results quoted[7] were somewhat variable, and that the specimen used[7] had been prepared by a method[8] involving crystallisation from ethanol, it appeared that the reported anomaly might be, in effect, a further example of solvent retention. If so, application of the infrared alkoxyl method[9] would reveal that ethyl iodide, and not methyl iodide, was the reaction product.

2,3-Dimethyl-2,3-diphenylbutane, prepared by Farmer and Moore's method,[8] was re-crystallised from ethanol. After drying in the normal way, the product had m.p. 118° (lit., 118–119°). Analysis (Weiler and Strauss, Oxford,) England gave %C = 90·51 %H =, 9·34; required, %C = 90·75, %H = 9·25. When treated with constant-boiling hydriodic acid, under the conditions described by Anderson and Duncan,[9] this compound gave no volatile reaction products, even after prolonged reflux overnight. Indeed, so stable is this hydrocarbon that it was recovered unchanged (identity of infrared spectrum) from the hydriodic acid reaction medium. This compound therefore neither retains solvent of crystallisation nor reacts anomalously under *normal* Zeisel conditions.

It is perhaps significant that Huang and Morsingh reported[7] that neither the dimethoxy derivative (I, X = OCH_3) nor compound II reacted anomalously, and that drastic conditions, normally reserved for the analysis of *N*-methyl groups, were used[10] in their analyses. Thus the sample was dissolved in phenol and acetic anhydride and refluxed with hydriodic acid; after evaporation to dryness, the residue was heated above 300°. It is quite unreasonable for results obtained by such a procedure to be described[10] as anomalous Zeisel methoxyl determinations.

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Summary—2:3-dimethyl-2:3-diphenylbutane is stable to reflux with constant-boiling hydriodic acid under standard Zeisel alkoxyl reaction conditions. A previous report that this compound reacts anomalously is therefore incorrect.

Zusammenfassung—2,3-Dimethyl-2,3-diphenylbutan ist stabil, wenn es unter Rückfluss mit konstantsiedender Salzsäure gemäss den Bedingungen einer Alkoxylbestimmung nach Zeisel gekocht wird. Eine frühere Mitteilung, dass die Verbindung abnormales Verhalten zeigt, ist daher unrichtig.

Résumé—Le 2-3-diméthyl-2-3-diphénylbutane est stable quand il est chauffé au reflux avec de l'acide iodhydrique bouillant constamment dans les conditions de la réaction standard de Zeisel pour les alcoyles. Un rapport antérieur prévoyant que ce composé réagit de facon anormale est donc incorrect.

* Part VII: *Talanta*, 1961, **9**, 611.

REFERENCES

[1] H. Gysel, *Mikrochim. Acta*, 1954, 743.
[2] D. M. W. Anderson and J. L. Duncan, *Chem. and Ind.*, 1959, 457.
[3] N. Karpitschka, *Mikrochim. Acta*, 1961, 738.
[4] D. M. W. Anderson and J. L. Duncan, *Talanta*, 1961, **8**, 241.
[5] D. M. W. Anderson and N. J. King, *ibid.* 1961,, **8**, 497.
[6] D. W. Drummond and E. E. Percival, *J. Chem. Soc.*, 1961, 3908.
[7] R. L. Huang and F. Morsingh, *Analyt. Chem.*, 1952, **24**, 1359.
[8] E. H. Farmer and C. G. Moore, *J. Chem. Soc.*, 1951, 141.
[9] D. M. W. Anderson and J. L. Duncan, *Talanta*, 1960, **7**, 70.
[10] R. L. Huang and L. Kum Tatt, *Analyt. Chem.*, 1955, **27**, 1030.

Talanta, 1962, Vol. 9, pp. 623 to 624. Pergamon Press Ltd. Printed in Northern Ireland

LETTER TO THE EDITOR

Separation of mercury by extraction with tri-n-butyl phosphate

SIR,

TRI-n-BUTYL phosphate (TBP) has become well-known as an agent for extracting inorganic species from aqueous solutions. The results of Ishimori *et al.*[1] indicate that mercury^{II} differs from many other elements in that it is extracted into TBP from very dilute hydrochloric acid. It seems, therefore, that TBP might prove useful for the separation of traces of mercury. We have measured the distribution coefficient

$$D = \frac{\text{Total } [Hg^{II}] \text{ in the equilibrium TBP phase}}{\text{Total } [Hg^{II}] \text{ in the equilibrium aqueous phase}}$$

for extraction from solutions of hydrochloric acid of different concentrations at 20°. ^{203}Hg (half-life 46·9 d) was utilised as a tracer in the partition measurements and was assayed by γ-scintillation counting. When a_0 and a were the count rates (corrected for background) of identical volumes of equilibrium organic and aqueous phases, respectively, then $D = a_0/a$. In Table I are shown results obtained with

TABLE 1. EXTRACTION OF Hg^{II} BY TRIBUTYL PHOSPHATE FROM HCl + H_2O

Initial concentration of Hg^{II} in aqueous phase $2{\cdot}3 \times 10^{-3}M$			Initial concentration of Hg^{II} in aqueous phase $4{\cdot}64 \times 10^{-2}M$		
Initial concn. of HCl in aqueous phase, M	D	E	Initial concn. of HCl in aqueous phase, M	D	E
0·01	61·2	98·6	0·01	52·9	98·4
0·142	77·1	98·9	0·66	63·8	98·6
0·33	117·8	99·3	1·32	71·2	98·6
0·61	122·4	99·3	1·98	123·4	99·3
0·66	131·1	99·3	2·64	107·8	99·2
0·99	108·6	99·2	3·31	168·1	99·5
1·65	152·6	99·4	3·64	156·8	99·5
1·85	171·1	99·5	3·95	159·4	99·5
2·37	189·8	99·5	3·97	144·5	99·4
2·38	195·6	99·5	4·30	175·1	99·6
2·62	208·5	99·6	4·63	147·1	99·5
2·64	224·0	99·6	4·97	143·3	99·5
2·91	217·6	99·6	5·28	107·3	99·3
3·57	173·3	99·5	5·95	104·7	99·3
3·83	220·2	99·6	6·60	66·5	99·0
3·96	194·8	99·6	7·94	49·1	98·7
4·10	134·7	99·4	9·26	26·4	97·8
4·54	139·1	99·4			
4·62	129·6	99·4			
5·15	136·2	99·5			
5·21	126·0	99·4			
5·85	130·1	99·5			
6·26	118·4	99·4			
7·12	91·0	99·3			
7·14	80·5	99·2			
7·26	61·5	98·9			
7·94	51·4	98·8			
9·23	30·4	98·0			
9·24	29·9	98·0			
10·59	16·1	96·5			
11·90	8·86	94·3			

Values of D are average from duplicate measurements.

initial aqueous solutions $2{\cdot}3 \times 10^{-3}$ and $4{\cdot}64 \times 10^{-3}M$ in Hg^{II}. If equal volumes of initial aqueous and organic phase are employed then the percentage extraction $E = 100\,DR/(1 + DR)$, where R is the ratio of the volume of the organic phase to the volume of the aqueous phase after equilibration.

The efficiency of separation of mercury from a number of other elements by the following procedure was tested using radiotracers. A solution of Hg^{II} in $0{\cdot}05M$ hydrochloric acid was equilibrated for several min with an equal volume of TBP. After centrifuging, the aqueous phase was withdrawn using a transfer pipette, and was equilibrated with a further portion of TBP. The organic layers were separated, combined, and washed for 5 min by agitating with a small amount of $3M$ hydrochloric acid. The TBP phase was then separated, and the mercury was removed from it as metal by stirring for several min with 5 ml of 50% hypophosphorous acid and centrifuging at high speed. The procedure gave yields of mercury greater than 99%. The percentage removal from the mercury of different elements present in tracer amounts was Co^{II} 100%, Mn^{II} 99·0%, Tl^{I} 100%, Cs 99·8%, Zn 99·6%. Moreover, in an experiment in which a solution of mixed fission products was added, 99·4% of the initial γ-ray activity was removed by the procedure.

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16 *March* 1962

REFERENCE

[1] T. Ishimori, K. Watanabe and E. Nakamura, *Bull. Chem. Soc. Japan*, 1960, **33**, 637.

Talanta, 1962, Vol. 9, pp. 625 to 626. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEWS

Quantitative Organic Microanalysis. AL STEYERMARK. Second Edition. Academic Press Inc., New York, 1961. Pp. xviii + 665. 118s.

THIS revised and enlarged edition of Steyermark's well-known book might be expected to have the same impact on microchemistry as the first edition had ten years ago. During this time many notable advances in organic analysis have been made and it is not unreasonable to expect that considerable attention would have been given to them in this new edition. Although it would be unfair to say that no mention is made of many of these developments, nevertheless the treatment given to them is generally quite inadequate and completely ridiculous for a book which sets out to be a standard work of reference.

The apparatus of organic microanalysis has provided a happy hunting ground for the many microanalysts who seek to establish uniformity of equipment and techniques. Several committees exist for the sole purpose of standardising the numerous pieces of apparatus; it is well-known, however, that such committees are invariably working against time—that new techniques and apparatus are always being devised to supplant, and often to render obsolete, the equipment and methods undergoing the laborious process of standardisation. While it is foolish to argue against the necessity for a certain amount of standardisation, to accept it as wholeheartedly as the author has apparently done is to introduce an attitude of complacency which is incompatible with the rapidly developing nature of the subject.

In the present text, the conservative approach of the many standardising committees with which the author is actively engaged is painfully evident. Few European laboratories employ the classical Pregl method for carbon and hydrogen and fewer would even contemplate the Carius methods for sulphur and halogens. Yet such methods are the author's choice, while modern procedures are virtually ignored.

The original edition appearing at an opportune time in the immediate post-war period was welcomed by those people who were caught up in the increased demand for routine organic microanalytical laboratories. Few contemporary texts provided the specifications for apparatus so necessary for those embarking on such projects for the first time. Today, this over-elaboration of detail concerning apparatus is of more value to the manufacturer of scientific apparatus than to the practising microanalyst to whom this book is largely addressed.

In conclusion, this book has missed the opportunity of retaining its original status. There is still much useful information to be found in it, but it is doubtful whether this will still appeal to the individualistic temperaments of many microanalysts.

WILLIAM I. STEPHEN

Qualitative Elemental Analysis. E. H. SWIFT and P. SCHAEFER. W. H. Freeman and Co., San Francisco, 1962. Pp. xiv + 469. $6.75

As one would expect of a book written by Dr. Swift, this is an excellent book from the standpoint of the objectives which the authors had in mind when writing it. They point out that a system of qualitative analysis is an effective means for systemisation and correlation of a large body of factual inorganic chemistry; that it provides a student with opportunities to apply chemical principles to laboratory problems; that it provides a useful means of showing the periodicity of chemical properties of the elements; and it teaches a great deal of laboratory technique.

The approach to qualitative analysis in this text is quite different from that of many contemporary texts in that it is a system for identification of *elements* rather than ions. For example, one identifies tin rather than stannous or stannic ion, and nitrogen rather than ammonium, nitrite or nitrate ion. While this approach is ably defended by the authors because it is useful, there are many instructors who will think that identification of ions is more important. The major portion of the system is devoted to metallic and amphoteric elements.

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The authors explain that this system is the outgrowth of a more complete system worked out for the Chemical Warfare Service in the early part of World War II. They believe that students will have greater interest in a system that was devised to solve actual problems in contrast to one that is only a system for teaching purposes. The emphasis is practical throughout the text rather than theoretical.

The book is divided into three sections:

Section I—Principles of Analytical Chemistry, 115 pages.

This section deals with the general theories involved in the system. It discusses schemes of qualitative analysis, definition of terms and units, reactions in homogeneous systems, redox reactions, reactions in heterogeneous systems, and periodic properties of the elements. Many instructors will no doubt think the treatment of topics is too brief and too limited. Such topics as activity of ions, ionic equilibria, chemical bonding, complex ions, and competing equilibria are given the briefest possible treatment—often only a paragraph. The discussion of acids and bases is almost entirely the Arrhenius concept, which is hardly in keeping with the more recent ideas of acid-base systems. However, it must be mentioned that additional theory is inserted in the laboratory portion when it is pertinent and timely.

Section II—Techniques of Analytical Chemistry, 57 pages.

This is an excellent description of the laboratory equipment and techniques employed in the system. The drawings are large, clear and descriptive. Correct and incorrect ways of doing things are shown very clearly.

Section III—The System of Analysis, 262 pages.

This section is obviously the largest and is devoted to the laboratory schemes of analysis. The laboratory directions are written very clearly and the many flow sheet and tabular outlines give a clear picture of each group separation, subgroup separation, and identification of each element.

The system is based on the suggestion that unknowns furnished to the students should be natural minerals or metallic alloys, although it provides for unknown solutions. Mineral samples are fused in nickel crucibles with a mixture of NaOH, $NaNO_3$ and Na_2CO_3. The melt is treated with water to separate it into a soluble and insoluble portion. The undissolved residue is called the *Basic Element Group* and contains compounds of Fe, Mn, Ti, the alkaline earths, Ag, Cu and Ni with traces of Pb and Sn. The solution contains the *Amphoteric Element Group* consisting of Pb, Cu, As, Sn, Al, Zn, Cr and V as well as the *Acidic Element Group* of I, Br, Cl, P, As, S and F. The solution is divided into two halves and each is treated differently. Separate samples are analysed for sodium and potassium, and for nitrogen and carbon.

Samples of alloys are dissolved in nitric acid if possible, or a mixture of nitric and hydrochloric acids. Directions are than given for separating the solution into three groups as outlined above for mineral samples.

If the sample is a solution it is evaporated to dryness and fused, as for minerals.

This system includes titanium and vanadium which are often omitted from many schemes of analysis but it omits antimony, bismuth, cadmium, and mercury which are usually included in other schemes of analysis.

Undoubtedly a student will learn a lot of chemistry and many useful laboratory methods from this system but its adoption will certainly mean a radical change for those who have been using conventional texts based upon the identification of ions. The very slight attention given to anions may be objectionable to some instructors.

A separate Teachers Manual is available to teachers. This manual gives much useful information on the use of the text, the time required for laboratory work, the preparation of solutions and sources of unknowns. There is also a very complete section on working problems and answering questions.

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Talanta, 1962, Vol. 9, pp. 627 to 629. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

(Material for this section should be sent directly to the Associate Editor)

BELGIUM

Friday–Saturday 14–15 *September* 1962: **Second Symposium on Chromatography:** *Belgian Society of Pharmaceutical Sciences.* Brussels.

Both theoretical aspects and practical applications of chromatography will be considered. A scientific exhibition will also be held. The official languages will be French, Dutch, English and German.

The Secretary's office of the Belgian Society of Pharmaceutical Sciences, 11 rue Archimède, Brussels 4, Belgium, will forward registration forms upon request, and registrations will be received until 1 August.

CZECHOSLOVAKIA

August 1962: **Spectroanalytical Methods for Extra Pure Substances:** *Association for Spectral Analysis:* Košice.

POLAND

Saturday 20 *October* 1962: **Symposium on Chromatography in Analysis and Preparation of Alkaloids:** *Chromatographic Subcommittee of the Analytical Chemistry Commission, Polish Academy of Sciences.* Poznań.

The address of the Organising Committee is Zaktad Chemii Ogólnej, University, Grunwaldzka 6, Poznań, Poland.

SWITZERLAND

Monday–Saturday 15–20 *October* 1962: **Second International Exhibition and Congress of Laboratory, Measurement and Automation Techniques in Chemistry.** Swiss Industries Fair, Basle (see *Talanta*, 1962, **9**, 401).

In connection with the Exhibition a **Technical Congress** will also be held, this being the 45th Meeting of European Federation of Chemical Engineering. The Congress will consist of a *Programme of Lectures on Automation in Chemistry*, which will constitute the 13th Meeting of the Swiss Federation of Automatic Control, and a *Programme of Lectures on Laboratory and Measurement Techniques*, organised by the Association of Swiss Chemists.

Full details of the *Programme of Lectures on Laboratory and Measurement Techniques* are as follows:

Thursday 18 *October—Separation Methods*

E. STAHL	*Entwicklung und Anwendung der Dünnschicht-Chromatographie.*
M. BRENNER	*Dünnschicht-Chromatographie: R_f-Wert und chemische Struktur.*
H. R. BOLLIGER	*Die Dünnschicht-Chromatographie der Vitamine.*
E. BAYER	*Präparative Gas-Chromatographie.*
R. S. EVANS	*Quantitative Aspects of Gas-Chromatography.*
H. SCHILDKNECHT	*Zonenschmelzen und Kolonnen-Kristallisieren, neue Trenn- und Reinigungsverfahren für kristallisierende Substanzen.*

Friday 19 *October—Determination of Particle Size*

A. PETERLIN	*Rheologische Methoden zur Bestimmung der Größe und Gestalt von Makromolekülen in Lösung.*
J. SADRON	*Optische Methoden zur Bestimmung der Größe und Gestalt von Makromolekülen in Lösung.*

Friday 19 *October—Methods for Determining Constitution and Structure*

J. D. DUNITZ	*Determination of Molecular Structure by X-Ray Methods.*
J. C. KENDREW	*X-Ray Methods in Protein Chemistry.*
J. D. WALDRON	*Appilcation of High Resolution Mass Spectrometry in Organic Chemistry.*
R. F. ZÜRCHER	*Neuere Anwendungen der magnetischen Kernresonanz-Spektroskopie.*

Saturday 20 *October*

A. HORSFIELD	*Recent Applications of Electron Spin Resonance in Chemistry.*
H. G. LEEMANN	*Konstitutionsermittlung mit Hilfe der Rotationsdispersion.*
B. BOEHLEN und A. GUYER	*Methoden der Mikrostrukturbestimmung poröser Stoffe.*

Recent Analytical Procedures

J. JORDAN	*Thermochemical Titrations.*
CH. WAKKER	*Analyse par fluorescence X, applications et limites.*
K. H. WAECHTER	*Das Beta-Gamma-Photometer als einfaches Hilfsmittel zur Elementaranalyse von organischen Substanzen und Lösungen.*

For further information apply to the Secretary's Office of ILMAC, Basle 21, Switzerland.

WEST GERMANY

Sunday–Friday 26–31 *August* 1962: **Thirteenth Session of the International Commission for Uniform Methods of Sugar Analysis.** Hamburg (see *Talanta*, 1962, **9**, 470).

UNGARN

Der Fachausschuss für Emissionsspektralanalyse der Materialprüfungsabteilung des Wissenschaftlichen Vereins für Maschinebau und seine Gruppe in Miskolc geben sich die Ehre, Sie davon zu unterrichten, dass die

V. Ungarische Tagung für Emissionsspektralanalyse

mit Kooperation der Gruppe des Wissenschaftlichen Vereins für Bergbau und Hüttenwesen in Diósgyör sowie mit Teilnahme der Technichen Universität für Schwerindustrie in Miskolc in der Zeit vom 9. bis 10. August in Miskolc stattfindet (*Talanta*, 1962, **9**, 402).

UNITED KINGDOM

British Standards Institution announces the following *New British Standard:*

B.S. 3483: 1962: *Methods for testing pigments for paints.* This describes, amongst other things, determination of matter volatile at 100°, determination of matter soluble in water, determination of acidity and alkalinity of aqueous extract, determination at 25° of pH of aqueous extract, determination of residue on sieve and determination of specific gravity. Price 8s.6d.)

The following *Amendment Slip* is also announced:

Addendum 1: 1960: *to B.S.* 2690: 1956: *Methods of testing water used in industry. Amendment No.* 2: *PD* 4548.

UNITED STATES OF AMERICA

Monday–Tuesday 6–7 *August* 1962: **Fifth Annual Rocky Mountain Spectroscopy Conference:** *Society for Applied Spectroscopy, Rocky Mountain Section.* Olin Hotel, Denver, Colo. (see *Talanta*, 1962, **9**, 546).

Wednesday–Friday 8–10 *August* 1962: **Eleventh Annual Conference on Applications of X-Ray Analysis:** *Denver Research Institute.* Albany Hotel, Denver, Colo.

Monday–Friday 13–17 *August* 1962: **Gordon Research Conference on Analytical Chemistry.** New Hampton School, New Hampton, New Hampshire (see *Talanta*, 1962, **9**, 405).

Tuesday–Friday 21–24 *August* 1962: **International Symposium on Far Infrared Spectroscopy.** Sheraton-Gibson Hotel, Cincinnati, Ohio.

Monday–Friday 27–31 *August* 1962: **Gordon Research Conference on Infrared Spectroscopy.** Kimball Union Academy, Meriden, New Hampshire (see *Talanta*, 1962, **9**, 405).

Wednesday 29 *August–Wednesday* 5 *September* 1962: **Fifth International Congress for Electron Microscopy:** *Electron Microscope Society of America.* Philadelphia.

Thursday–Saturday 1–3 *November* 1962: **Annual Southeastern Regional Meeting of American Chemical Society:** *American Chemical Society, East Tennessee Section* and *Oak Ridge National Laboratory.* Gatlinburg, Tennessee.

GLENN T. SEABORG, Chairman of U.S. Atomic Energy Commission, will present the opening address. In addition to general sessions in various fields of chemistry, symposia will cover Organic Reaction Mechanisms; Coordination Compounds; Radiochemical Techniques in Analytical Chemistry; DNA, RNA and Protein; and Application of High Speed Computors to Chemical Problems.

Further information may be obtained from Dr. F. A. GRIFFITTS, Maryville College, Maryville, Tennessee, U.S.A.

Monday–Friday 4–8 *March* 1963: **Fourteenth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy:** *American Chemical Society, Pittsburgh Section, Analytical Chemistry Group* and *Spectroscopy Society of Pittsburgh.* Penn-Sheraton Hotel, Pittsburgh, Pennsylvania.

Approximately 190 papers on all phases of analytical chemistry and spectroscopy will be presented. A symposium entitled *Solution Techniques in X-Ray and Emission Spectroscopy* will be cosponsored with the Society for Applied Spectroscopy. The Coblentz Society is coarranging a symposium on *Techniques related to Infrared Spectroscopy.* Additional symposia with the titles *Nuclear Magnetic Resonance—Nuclei other than Hydrogen, Gas Chromatographic Analysis of Metallo-Organics and Related Compounds, Uses of Reaction Rates in Analytical Chemistry* and *The Analysis of Refractory Metals* will also be held.

Original papers on all phases of analytical chemistry and spectroscopy are invited. A brief abstract (150 words) of each paper will be printed with the programme. Three copies of this abstract, with a letter listing the names of the authors, the laboratory in which the work was done, and the current addresses of the authors, should be addressed to: Dr. WILLIAM A. STRAUB, Programme Chairman, Fourteenth Pittsburgh Conference, Applied Research Laboratory, United States Steel Corporation, Monroeville, Pennsylvania, U.S.A. The final date for receipt of abstracts is 15 October 1962. One copy of the complete paper must be submitted by 1 January 1963.

In addition to the programme of technical papers there will be an exhibition of the newest analytical instrumentation, and a complete programme of activities for wives and lady attendees at the Conference is planned.

The **Fourth Omnibus Conference on Experimental Aspects of Nuclear Magnetic Resonance Spectroscopy** will be held at Mellon Institute, Pittsburgh, from Thursday 28 February to Saturday 2 March 1963, the week preceding the Pittsburgh Conference. The first day will be devoted primarily to broad-line work, the second to experimental developments of general interest and the third to high resolution techniques. For the convenience of those wishing to attend both meetings the Nuclear Magnetic Resonance sessions of the Pittsburgh Conference will be scheduled for Monday 4 March.

National Bureau of Standards has developed sets of colour standards to check the performance of spectrophotometer-tristimulus integrator combinations, the automatic recording and computing devices used in routine colour measurement. Each set consists of five 2-inch square filters made of selenium orange-red, signal yellow, sextant green, cobalt blue, and selective neutral glass. A detailed report issued with the standards contains instructions for their use as well as colorimetric data which aid in detecting errors inherent in the equipment and in making adjustments to correct for such errors.

ERRATA—VOLUME 9

Page 295: the journal in reference 2 should read *Ind. Eng. Chem.*

Page 355, title, Summary, first paragraph and under Reagents: for *5-(3-nitrophenylazo)salicylate* read *5-(4-nitrophenylazo)salicylate.*

Page 359, Fig. 5: for *5-(3-nitrophenylazo)salicylate* read *5-(4-nitrophenylazo)salicylate;* also, the nitrophenylazo group should be shown in the 5-position and not in the 4-position.

Page 363, Zusammenfassung: for *5-(3-nitrophenylazo)salizylsäure* read *5-(4-nitrophenylazo)salizylsäure.*

Page 364, Résumé: for *5-(3-nitrophénylazo)salicylique* read *5-(4-nitrophénylazo)salicylique.*

Page 452, second paragraph of Introduction: the reagent should read *N-(1-naphthyl)ethylenediamine dihydrochloride.*

Page 457, caption to Fig. 1: the final sentence should read *Reagent solutions contain 2.5 × 10^{-5} mole of $Cu(NO_3)_2$ [or $CuCl_2$] and 8.5 × 10^{-5} mole of di-octen in hexone medium.*

Talanta, 1962, Vol. 9, p. 630. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Spectrophotometric study of the thorium complex of B-SNADNS-6: SACHINDRA KUMAR DATTA and SACHINDRA NATH SAHA. (3 *May* 1962).

"Complexan Buffer": A new concept useful in theoretical consideration of equilibria involving complexans: MOTOHARU TANAKA. (4 *May* 1962).

New Redox Systems—V: Oxidation of uranium^{IV} with iron^{III} in 1,10-phenanthroline solutions: Indirect colorimetric determination of uranium: FRANTIŠEK VYDRA and RUDOLF PŘIBIL. (4 *May* 1962).

Effect of initial pH, phosphate and silicate on the determination of aluminium with aluminon: PA HO HSU. (10 *May* 1962).

Polarography of silver: R. M. DAGNALL and T. S. WEST. (10 *May* 1962).

Determination of amines by indirect bromination with chloramine-T: K. S. PANWAR, J. N. GAUR and N. K. MATHUR. (11 *May* 1962).

Assay of solutions for plutonium content by X-ray counting: W. R. DIGGLE and D. L. O. HUMPHREYS. (15 *May* 1962).

Chelate formation between thorium$^{(IV)}$ and sulphodichlorohydroxydimethylfuchsin dicarboxylic acid (trisodium salt): Studies on the composition and stability of the chelate and analytical applications of the reaction: SURESH C. SRIVASTAVA, SURENDRA NATH SINHA and ARUN K. DEY. (17 *May* 1962).

Die Bestimmung kleiner Fluormengen—III: Übersicht der Problematik der Bestimmung von Fluor und eine Konzeption der theoretischen analytischen Chemie: ROMAN VALACH (19 *May* 1962).

Untersuchungen an Reagenzien für Niob und Tantal: G. ACKERMANN and S. KOCH. (21 *May* 1962).

Determination of metals in metal chelate compounds: YUICHI TSUCHITANI, YUKO TOMITA and KEIHEI UENO. (22 *May* 1962).

New spectrophotometric methods for the determination of rhenium: D. I. RYABCHIKOV and L. V. BORISOVA. (28 *May* 1962).

Talanta, 1962, Vol. 9, pp. 631 to 637. Pergamon Press Ltd. Printed in Northern Ireland

THE COLORIMETRIC DETERMINATION OF MOLYBDENUM WITH POLYHYDRIC PHENOLS

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(*Received* 26 *November* 1961. *Accepted* 8 *March* 1962)

Summary—The use of polyhydric phenols as colorimetric reagents for molybdenum is reviewed. It is shown that any polyhydric phenol having two *ortho* hydroxyl groups can be used with equal success. The use of gallic acid or sodium 2,3-dihydroxynaphthalene-6-sulphonate has been discussed in greater detail. The practical sensitivity for molybdenum is about 0·1 μg/ml at 400 mμ.

A NUMBER of polyhydric phenols have been used as colorimetric reagents for molybdenum. It is proposed, in this paper, to show that polyhydric phenols in which there are two *ortho* hydroxyl groups may be generally used for this purpose.

Weinland and Gaisser[14] found that on treating ammonium molybdate with catechol in aqueous solution a deep red colour was produced. In neutral solution this colour arises from the formation of a chelate which requires two molecules of catechol to one of molybdenum[2,3,4,7] and is formed by any simple *ortho* dihydroxy phenol.[2,4,7] Catechol has been used for the detection[6] and determination[9] of molybdenum. Similar use has been made of pyrogallol,[1] Tiron (disodium 1,2-dihydroxybenzene-3,5-disulphonate),[15] 3,4-dihydroxybenzaldehyde[10] and tannic acid.[11,12] Halmekoski[5] used the reaction to determine catechol in the presence of excess molybdate.

Seifter and Novic[9] used a mildly alkaline (0·4% NaOH) catechol reagent which had to be stabilised with sodium metabisulphite. The colour obtained showed maximum absorption at 400 mμ, though a wide range of molybdate concentration[5] could be determined by a suitable choice of wavelength (up to 515 mμ). The sensitivity at 400 mμ was such that 1 μg of molybdenum per ml caused an optical density increase of 0·05. Beer's law was obeyed in the presence of a large excess of catechol and the colour was stable for 2 hours. Considerable interference was caused by iron^{III} but none was evident from cobalt or manganese. A more critical approach to the reaction was made by Haight and Paragamian,[3] who found complications when sodium sulphite was substituted for metabisulphite as stabiliser. The reasons given for this are not very convincing, and, moreover, a correct choice of conditions can eliminate the need for a stabiliser.

Will and Yoe[15] used Tiron as their reagent and carried out a thorough study of the optimum conditions. The maximum absorption occurred at 390 mμ and Beer's law was obeyed in the presence of a large excess of the reagent. The optimum pH range of 6·5–7·5 was obtained by using a suitable buffer. The colour became slightly more intense (by 1%) over the first 6 hours, but then became completely stable and remained unaffected by temperature (15–45°). At 390 mμ, 1 μg/ml of molybdenum caused an increase in optical density of 0·07, and a practical sensitivity of 0·1 μg per ml was claimed. The effects of a large number of ions on the system were investigated and methods were suggested for determining molybdenum in various materials.

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The present authors have studied the reaction with twelve suitable phenols, which are listed in Table I together with data on the solvent needed to prepare a 1% solution and the discoloration produced by aerial oxidation. A more detailed study of the nature of these complexes has been published elsewhere.[2]

Any one of these phenols can be used as the colorimetric reagent. In the presence

TABLE I.—SOLVENTS FOR POLYHYDRIC PHENOLS.

No.	Phenol	Solvent for 1% solution	Colour of solution	Colour after 24 hr
I	Catechol	Water	Colourless	Pale yellow–pink
II	4-Methylcatechol	Water	Slightly yellow	Yellow–pink
III	3,4-Dihydroxybenzaldehyde	Water	Pale yellow–brown	Yellow–brown
IV	3,4-Dihydroxybenzoic acid	Water	Slightly yellow	No change
V	Tiron	Water	Colourless	No change
VI	Gallic acid	20% aqueous ethanol	Colourless	No change
VII	Pyrogallol	Water	Colourless	Yellow
VIII	2,3,4-Trihydroxybenzoic acid	20% aqueous ethanol	Slightly yellow	No change
IX	3-Methyl-6-sec-propylcatechol	30% aqueous ethanol	Yellow	Darker
X	4-Butylcatechol	30% aqueous ethanol	Yellow	Darker
XI	2,3-Dihydroxynaphthalene	20% aqueous ethanol	Slightly pink	No change
XII	Sodium-2,3-dihydroxynaphthalene-6-sulphonate	Water	Colourless	Very pale pink

of a large excess of the reagent (phenol:Mo > 25:1), Beer's law is applicable (*vide infra* and ref. 2). At a given pH and a given wavelength (in the range 400–550 mμ) the sensitivity for molybdenum is similar. The presence of up to 50% of ethanol or acetone as mutual solvents does not change the optical density. This applies for the concentrations of molybdenum normally employed in colorimetric analysis. In more concentrated solution (0·01 *M*), molybdate forms a yellow coloration in 50% alcohol or acetone; a more complete study of this reaction is being published elsewhere.

The main objection to the use of many of these phenols is their poor colour stability in aqueous solution, but this may be overcome by using freshly prepared reagent or by stabilising, either by acidifying or with sodium sulphite. Acidifying with acetic acid to a pH around 4·5 will effectively stabilise the reagent. A second

objection to some of the phenols mentioned may be their relatively high price, but if an urgent molybdenum determination is required it is probable that at least one of the phenols mentioned will be available in the laboratory.

Gallic acid (VI) and sodium 2,3-dihydroxynaphthalene-6-sulphonic acid (XII) are stable in aqueous solution and are inexpensive; they have been chosen as examples for a more detailed description.

EXPERIMENTAL

Apparatus and reagents

Colorimetric measurements were made with a Hilger "Spekker" absorptiometer and a Unicam SP 600 spectrophotometer. Measurements of pH were carried out with a glass/calomel electrode system in conjunction with a Pye Universal pH meter.

Phenol solutions: 1% solutions of phenol VI and phenol XII were prepared from the commercially available solids without further purification. Phenol VI was dissolved in warm 20% aqueous ethanol, whilst phenol XII was dissolved in boiling water. On cooling, the solutions remained clear, but were filtered to remove any suspended matter.

Buffer solutions: Since the final colour was fairly sensitive to changes in pH the solutions had to be suitably buffered. Three buffer systems were used: (i) acetic acid–sodium acetate; (ii) potassium dihydrogen phosphate–caustic soda; (iii) potassium hydrogen phthalate–caustic soda. The concentrations used were such that on diluting the final solution the usual working strengths ($\sim$0·05M) were obtained. Various solutions were prepared according to the pH required; the quantities needed may be found in any suitable reference work (*e.g.*, Vogel[13]).

Standard molybdate solutions: two standard solutions were used from which all the working solutions were prepared:

(1) 3·9640 g of dried AnalaR sodium molybdate were dissolved in water and diluted to 1 litre. This solution contained 0·001 g/ml of molybdenum.

(2) 1·8401 g of dried AnalaR ammonium paramolybdate were dissolved in water and diluted to 1 litre. This solution also contained 0·001 g/ml of molybdenum.

Both solutions were checked by a gravimetric determination with 8-hydroxyquinoline and found to be correct and with identical molybdenum concentrations. On application of the colorimetric method, the two solutions gave identical results. The ammonium molybdate turned yellow on ageing (clear glass bottle) whilst the sodium molybdate solution remained clear and colourless.

Absorption spectra of the complexes

The absorption spectra of the complexes formed by phenols VI and XII were compared under identical conditions and are shown in Fig. 1. Both molybdate and the free phenols have negligible optical density under the same conditions in the wavelength range shown. To obtain full development of the colour, at least 10 ml of 1% reagent solution were required in each case. Fig. 2 shows the variation of optical density at 400 mμ with increasing reagent concentration, for a solution containing 10 μg of molybdenum per ml.

Fig. 3 shows the variation of optical density with molybdenum concentration at two wavelengths. The straight lines indicate that Beer's law is applicable. It will be noted that by a suitable choice of wavelength a wide range of molybdenum concentrations can be covered.

Sensitivity

Using a 1-cm optical path, the practical sensitivity for both reagents is about 0·1 μg/ml of molybdenum, which is similar to that given in the works already discussed.[9,15]

Effect of pH variation

Variations in pH were brought about by altering the composition of the buffer used. Fig. 4 shows the effect of differing buffers on the optical density of the solutions. For phenol VI the optimum pH appears to be between 6·5 and 7·0. At lower pH values the optical density falls steadily, being halved at pH 4·0. At pH values above 7·0, oxidation of phenol VI occurs very quickly, leading to false results. For phenol XII the optimum pH is better defined, and falls between 6·5 and 8·0. At pH values greater than 8·0 the reagent itself turns pink and causes interference. It is noteworthy that identical results were obtained from different buffer systems.

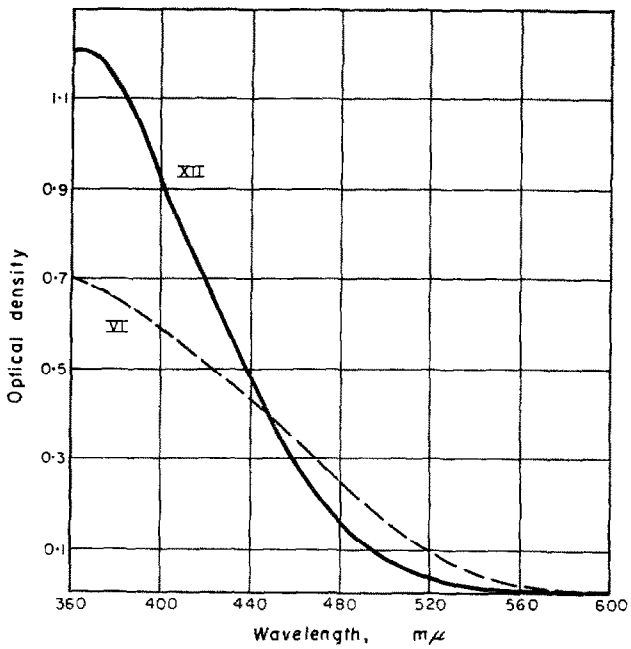


FIG. 1.—Absorption spectra of solutions containing 10 μg/ml of molybdenum and 0·002 g/ml of polyhydric phenol, buffered at pH 5·1 with acetic acid-sodium acetate.
– – – Gallic acid.
—— Sodium-2,3-dihydroxynaphthalene-6-sulphonate.

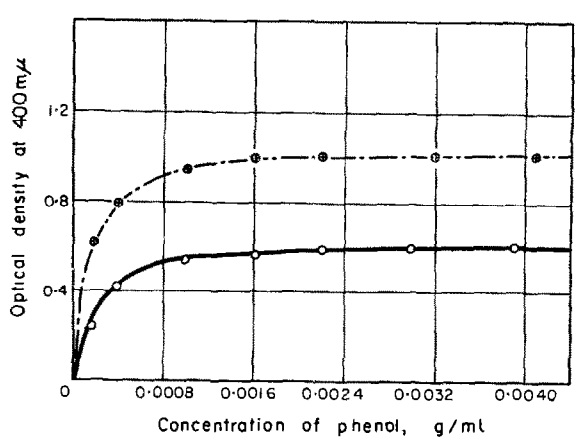


FIG. 2.—Variation of optical density at 400 mμ with concentration of polyhydric phenol. Solutions contain 10 μg/ml of molybdenum, buffered to pH 5·1 with acetic acid-sodium acetate.
○—— Gallic acid.
⊕– · – Sodium-2,3-dihydroxynaphthalene-6-sulphonate.

Fig. 4 also shows the stability of the colour with time. Phenol VI is only stable in rather acid solutions whilst phenol XII is stable below pH 6·5. To use pH ranges in which the colours are completely stable would result in a loss of sensitivity. A useful compromise is to have the pH between 5 and 6 when phenol VI is stable for a few hours and phenol XII is completely stable.

Order of adding reagents and temperature stability

Varying the order in which the reagents were added made no significant difference to the results. If the phenol was added to the molybdate and the addition was followed by pH adjustment, it took a few min before the colour became stable, depending on the conditions. It was found most convenient to add first the buffer and then the phenol to the molybdate solution, in which circumstances

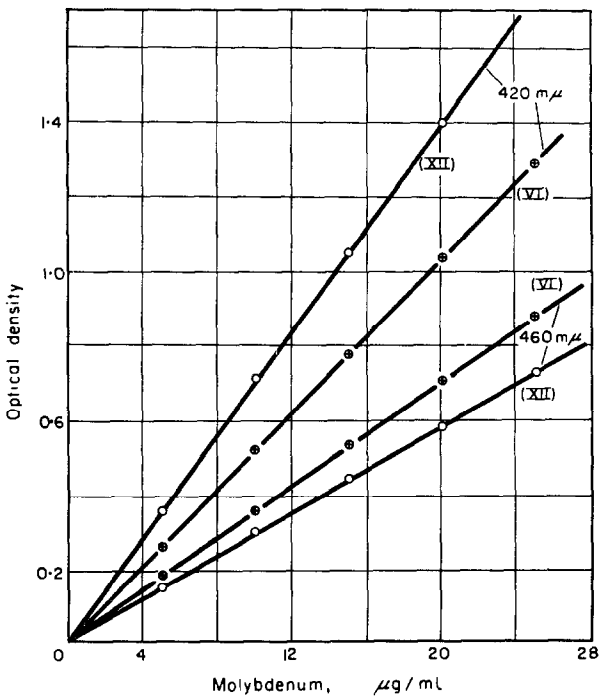


FIG. 3.—Applicability of Beer's law. Solutions contain various concentrations of molybdate in the presence of 0·002 g/ml of polyhydric phenol (Table I); buffered at pH 5·1 with acetic acid–sodium acetate.

the full colour development was practically instantaneous. In all cases the development of the colour was complete within a few min and the optical density remained constant in the temperature range 10–50°.

Effect of diverse ions

This aspect was thoroughly examined by Will and Yoe[15] in connection with Tiron, and it was found that the same ions generally interfered in the reaction with other polyhydric phenols. Those authors obtained interference by a variety of common ions such as Al^{3+} and Mg^{2+}, through precipitation of their hydroxides at pH values above 7. Such interference can easily be eliminated by using a lower pH, without any great loss in sensitivity. The only common ions which form coloured complexes with the phenols are Fe^{3+}, OsO_5^{2-}, Cu^{2+}, WO_4^{2-}, UO_2^{2+}, VO_2^{3+} and Ti. The molybdate ion can readily be separated from these ions (excepting WO_4^{2-} and OsO_5^{2-}) by passing the solution through a cation exchanger (Zeo-Karb 225) in the hydrogen form. This yields a solution of molybdic acid[8] which can be converted back to the simple molybdate by adjusting the pH with sodium hydroxide. Interference by tungstate is dependent on the pH and wavelengths used. At pH 7 the interference is negligible at wavelengths above 400 mμ but at pH 4 wavelengths above 430 mμ must be used. The

method recommended by Will and Yoe,[15] in which the Mo is first separated as the complex with α-benzoinoxime, is equally good but slightly more tedious. Common anions such as halides, nitrate, sulphate, oxalate, tartrate and those used in the buffer solutions do not interfere with the colour development.

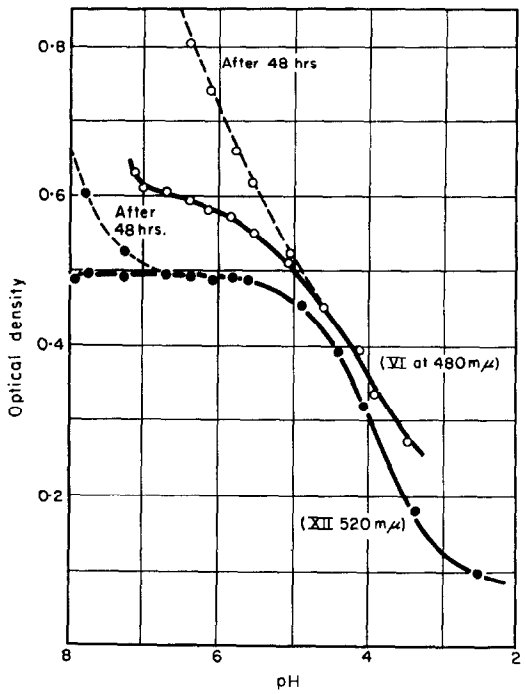


FIG. 4.—Variation of optical density with pH and time. Solutions contain 10 μg/ml of molybdenum and 0·002 g/ml of polyhydric phenol, with buffers of varying pH.

Recommended Method

Reagents

(1) *Polyhydric phenol:* A 1% solution in water or aqueous alcohol, using the purest available grade. Old or discoloured samples are best decolorised by treating a fairly concentrated alcoholic solution with activated charcoal, followed by filtering and diluting with water.

(2) *Standard molybdate:* 3·964 g of dried AnalaR sodium molybdate dissolved in water and diluted to 1 litre, giving a solution containing 0·001 g/ml of Mo. If other grades of molybdate are used these should be assayed for molybdenum by one of the standard methods.

(3) *Buffer solution:* A suitable buffer giving pH ~5·2 may be prepared by dissolving 109 g of hydrated AnalaR sodium acetate (or an equivalent amount of the anhydrous material) in 500 ml of water, adding 10 ml of glacial acetic acid, and diluting to 1 litre.

Method

The sample is dissolved by one of the usual methods, *e.g.*, fusion, mineral acids or alkali. If any reduction of the molybdenum occurs it should be oxidised back to Mo^{VI} with concentrated nitric acid. The interfering ions are removed by one of the methods already mentioned, and the concentration of the solution is so adjusted that 5 ml contains 5–100 μg/ml of Mo. A 5-ml portion of the solution is transferred to a 25-ml graduated flask and the pH is adjusted to be as near as possible to that of the buffer solution. Five ml of the buffer solution and 10 ml of the polyhydric phenol solution are added and the volume is made up to the mark with water. The optical density of the solution is measured at 420 mμ (or with a blue filter in the case of a colorimeter) and compared with a calibration curve prepared from the standard molybdate solution. By making the optical measurements at longer wavelengths (500–600 mμ) the sensitivity can be decreased so that higher molybdate concentrations may be determined.

The present authors have used this method satisfactorily to determine the molybdenum in small quantities of various solid molybdates and heteropolymolybdates of unknown composition as well as in waste liquors containing small quantities of molybdenum.

Zusammenfassung—Die Anwendung polyhydrischer Phenole als Reagensien fur Molydän wird zusammenfassend behandelt. Es wird gezeigt, dass jedes polyhydrische Phenol mit zwei Hydroxylgruppen in Orthostellung erfolgreich verwendet werden kann. Die Verwendung von 3,4,5-Trioxybenzoesäure und 2,3-Dioxynaphthalin-6-sulfonate wird im Detail behandelt. Die Empfindlichkeit ist *ca.* 0·1 μg Mo/ml bei 400 mμ.

Résumé—Les auteurs passent en revue l'utilisation des phénols polyhydriques comme réactifs colorimétriques du molybdène. Ils montrent que tout phénol polyhydrique ayant deux groupes hydroxyle en ortho peut être employé avec une égale réussite. L'utilisation de l'acide gallique et du 2,3-dihydroxynaphthalène-6-sulfonate de sodium a été discutée en détail. La sensibilité pratique pour le molybdène est d'environ 0,1 μg par ml à 400 mμ.

REFERENCES

[1] R. I. Alekseev, *Zavodskaya Lab.*, 1938, **7**, 863.
[2] H. Buchwald and E. Richardson, *J. Inorg. Nucl. Chem.*, 1960, **15**, 133.
[3] G. P. Haight and V. Paragamian, *Analyt. Chem.*, 1960, **32**, 642.
[4] J. Halmekoski, *J. Ann. Acad. Sci. Fennicae*, 1959, **A 11**, 96.
[5] *Idem, Suomen. Kem.*, 1959, **B 32**, 274.
[6] A. Martini, *Mikrochemie*, 1928, **6**, 63; 1932, **12**, 112.
[7] J. C. McGowan and P. W. Brian, *Nature*, 1947, **159**, 373.
[8] E. Richardson, *J. Inorg. Nucl. Chem.*, 1959, **9**, 267.
[9] S. Seifter and B. Novic, *Analyt. Chem.*, 1951, **23**, 188.
[10] M. Shapiro, *Zhur. analit. Chim.*, 1951, 6, 371; *Chem. Abs.*, 1952 **46**, 2956a.
[11] G. Spurge, *Chem. Eng. Min. Rev.*, 1919, **11**, 258.
[12] O. Steiner, *Z. analyt. Chem.*, 1930, **81**, 389.
[13] A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*. Longmans Green and Co., London, 1953, pp. 868-872.
[14] R. F. Weinland and F. Gaisser, *Z. anorg. Chem.*, 1919, **108**, 231.
[15] F. Will and J. H. Yoe, *Analyt. Chim. Acta*, 1953, **8**, 546.

Talanta, 1962, Vol. 9, pp. 639 to 645. Pergamon Press Ltd. Printed in Northern Ireland

EMISSION SPECTRA FROM HIGH-FREQUENCY EXCITATION—III*

A STUDY OF ARGON-CARBON DIOXIDE MIXTURES

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Summary—A continuous discharge at 230 megacycles, produced by a radio-frequency extra-hightension generator, in a sealed-off gas system, has been used in conjunction with a quartz prism spectrophotometer to study binary mixtures of argon and carbon dioxide. The concentrations of mixtures in the range 9 to 90% argon, and 91 to 10% carbon dioxide have been determined with a reproducibility of ±3.2% absolute, expressed as a standard deviation. Determinations can be carried out in about 1 min, making the technique superior to the usual spectrographic technique. The procedure developed suggests that with improved instrumentation, ensuring constancy of source intensity, and substitution of a continuously flowing gas for the sealed-off system, it might be possible to extend the technique to mixtures of other gases and obtain better reproducibility and accuracy.

INTRODUCTION

A PRELIMINARY survey[1] of the emission spectra of some inorganic gases excited by high-frequency discharge indicated the possibilities of optical spectroscopy with photoelectric measurement in place of conventional photographic spectroscopy, for quantitative analysis of gas mixtures. The need for rapidity in intensity measurement makes the use of photoelectric measurement preferable to the photographic techniques, especially in the case of gases which are dissociated under the discharge (*e.g.* $CO_2 \rightarrow CO$) and can, therefore, be determined satisfactorily by this technique only when measurement is almost instantaneous. The photoelectric technique eliminates tedious plate calibrations and other time-consuming processes which are integral parts of the photographic technique, thereby resulting in greater speed. It also ensures greater reproducibility and accuracy, since the reproducibility and accuracy of the photographic technique is based on many variables, especially the behaviour of photographic emulsions.

This paper presents results obtained using a radio-frequency high-tension generator in conjunction with a quartz prism spectrophotometer for the study of binary mixtures of argon and carbon dioxide.

EXPERIMENTAL

Apparatus

The apparatus consists of three separate units:

(*i*) A high-vacuum train with a sealed-off gas system, all constructed from borosilicate glass. Figs. 1 and 2 are schematic diagrams of the high-vacuum system and the discharge cell, respectively. C and E are two 5-litre flasks. Argon is admitted through a mercury-bubbler, A, and the cold trap B. Carbon dioxide is admitted from the test tubes T_1 and T_2, after condensation and distillation. D is a 1-litre flask used as a reserve bulb for storage of gas mixtures. M is a vacuum-type mercury-manometer; P is a Pirani gauge; F is a cold trap to Reep mercury and water vapours from the discharge cell; I is a two-stage mercury-diffusion pump backed by a rotary oil pump, J, combined performance of which gives a vacuum of $\simeq 10^{-4}$ mm of mercury in about 0·5 hr. X is the discharge cell of borosilicate glass with a sealed-on quartz window on the side facing the monochromator assembly. This discharge cell has the following dimensions: overall length 8·2 cm, internal diameter

* Part II—See ref. 1.

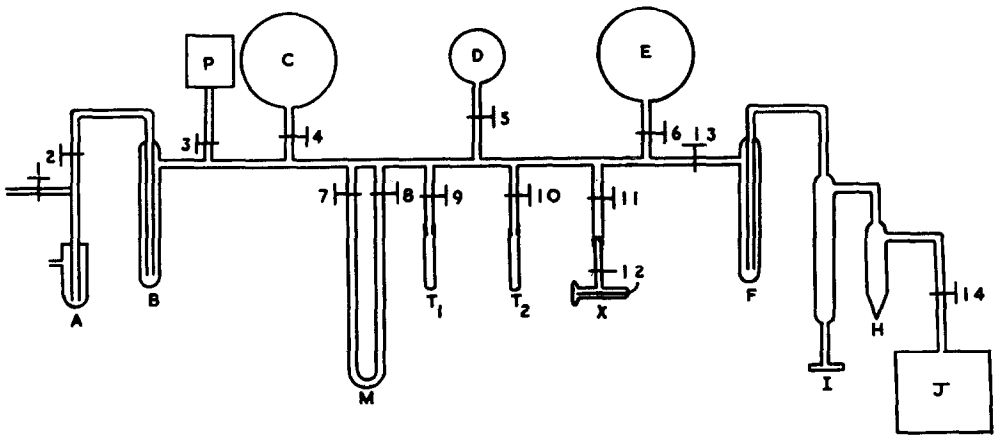


FIG. 1 Schematic diagram of high vacuum train with discharge cell

A	Mercury bubbler	T_1, T_2	Test tubes
B, F	Cold traps	J	Rotary oil pump
C, E	5-litre flasks	X	Discharge cell
D	1-litre flask	1–14	Vacuum taps
H	Mercury trap	P	Pirani gauge
I	Mercury diffusion pump	M	Vacuum type mercury-manometer

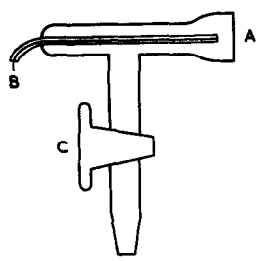


FIG. 2..—Schematic diagram of discharge cell
A Quartz window sealed on.
B Tungsten electrode, glass-coated.
C Vacuum tap.

about 1 cm in the body and 2 cm at the quartz window. The quartz window is 1 mm thick, and the electrode is a glass-coated tungsten wire, diameter 1 mm.

(*ii*) A radio-frequency extra-high tension generator operating at about 230 megacycles for excitation. Details of this apparatus have been described elsewhere.[2] This generator has an output tuned by a variable capacitor. Discharge intensity is controlled by varying the capacitance.

(*iii*) A Hilger "Uvispek" photoelectric spectrophotometer with a quartz prism. Preliminary studies were carried out with the Hilger medium quartz spectrograph, E.498.

Gases

Argon: This gas was obtained from cylinders of normal commercial supply, of rated purity not less than 99·95%. It was used without further purification.

Carbon dioxide: This gas was obtained from the normal commercial supply of "Drikold", of rated purity 99·8%. It was further purified by repeated condensation and distillation using liquid nitrogen.

Gas mixing technique

The high vacuum train is pumped down to a vacuum of 10^{-4} mm of mercury. The gases for calibration mixtures are then admitted separately, one into the flask C and the other into the flask E, at pre-determined pressures. The gases are mixed in one of these flasks, by admitting the second component into it with a high backing pressure to prevent diffusion of the first component from the

mixing flask. When there is high backing pressure, mixing is fast. The mixture is left for several hr before use.

The compositions of the mixtures are determined by the partial pressures of the two components as measured at the time they are admitted, in quick succession, into the mixing chamber, at room temperature, thus eliminating the need for calibration of the volumes of the apparatus. Either the flask C or E can be used as the mixing chamber and the other as reservoir for the diluent gas. To prepare mixtures of known composition ranging from 1 to 99% of each component, it is necessary to create a pressure differential between the gas in the mixing chamber and the diluent gas in its reservoir at the time of admission of the diluent gas into the mixing chamber. An adequate pressure differential is created by maintaining the pressure of the gas in the mixing chamber at a low level relative to the high backing pressure of the diluent gas in its reservoir. This is accomplished, for a 50:50 mixture, by maintaining, before mixing, a pressure of say, 20 cm of mercury in the mixing chamber and 60 cm of mercury in the diluent gas reservoir. To prepare other mixtures, it is necessary to have progressively higher pressures in the diluent gas reservoir as the concentration ratio departs from the 50:50 ratio. The positions of the two components in respect of the mixing chamber and the reservoir are reversed as the concentration ratio crosses the midpoint, *i.e.* 50:50, of the scale of concentration ratios.

This mixing technique introduces several minor errors: *e.g.*, (1) an error in the measurement of gas pressures with the mercury manometer; (2) an error arising from change in temperature in the mixing chamber during the mixing process; (3) the diffusion of minute quantities of the component gases out of the mixing chamber during the mixing process; (4) selective adsorption of one component of the mixture on the glass surface of the mixing chamber.

The combined effect of all these errors is to introduce into the calibration mixture an uncertainty in the exact value of the concentrations.

Preliminary studies

Preliminary studies of the mixtures were made with the quartz spectrograph, using a slit-width of 0·03 mm, an exposure time of 15 min, Ilford panchromatic HP3 plates, and a copper arc for calibrating wavelength. The object was to select those lines and band-heads which are present in the spectra of mixtures of varying concentrations and are not affected by impurity bands. The range covered by this study was from 99·0% Ar and 1·0% CO_2 to 0·9% Ar and 99·1% CO_2. Fig. 3 is a photograph of the spectra of a mixture containing Ar 15·0% and CO_2 85·0%. The examination of the spectra reveals the following points: (*i*) The atomic lines of Ar are present; and (*ii*) CO_2 produces very strong and persistent bands with band-heads at λ 2883 Å and λ 2896 Å, probably produced[3] by the ionised molecule CO_2^+; and also carbon monoxide bands as a result of dissociation into carbon monoxide caused by the discharge. The colour and intensity of the glow alter as the discharge continues to pass.

For calibration purposes the Ar line at λ 2942·9 Å and the CO_2^+ band, a very strong and persistent one with the band-head at λ 2896 Å, were finally selected from the many lines and band-heads examined. It may be seen from the spectra that these lines and band-heads are free from interference by impurity bands. The CO_2^+ band-head at λ 2896 Å has been used by several workers[4] for the quantitative determination of CO_2 in respiratory gases by spectrophotometric measurement of emission intensity.

This final selection was based on results obtained by examining the ratios of peak line or band-head intensities at different wavelengths for mixtures of varying concentrations. The intensity ratios were measured spectrophotometrically and their values were plotted as a function of concentration ratios, using a logarithmic scale in both cases.

Spectrographic detection limits

The spectrographic detection limits were established experimentally by photographing the spectra of mixtures of different compositions on the same photographic plate, and examining the spectra with a magnifying lens against an illuminated background, to assess the concentration sensitivity of the lines and the band-heads for analytical purposes.

This study established that the lowest limits of detection of Ar and CO_2 in their mixtures, using the Ar line at λ 2942·9 Å and the CO_2 band–head at λ 2896 Å, are of the order of 1%. Therefore, the study of the mixtures has been limited to concentrations of 1% to 99%.

Procedure

The high vacuum train with the discharge cell in position, is pumped down to a pressure of 10^{-4} mm of mercury while subjected to prolonged baking with a naked flame in order to outgas the system. The gases are then admitted and mixed in the mixing chamber. The train is again pumped down to 10^{-4} mm. The sample of the mixture is admitted into the discharge cell and the discharge is switched

on. The pressure of the sample is reduced and the sample is isolated at a line-pressure of 0·50 mm, measured with a Pirani gauge. The discharge is started, and with the sample glowing, the spectrophotometer slits are opened to 0·50 mm (*i.e.*, 5 Å) The variable condenser of the generator is adjusted until the glow gives the maximum signal at the preselected wavelength. Fine adjustment of the setting of the wavelength drum is made by slowly turning the wavelength drum until maximum signal is registered. The measurement of peak intensities is immediately made; any unavoidable time-lag between the switch-on of the discharge and the measurement is kept at a minimum and is constant for all determinations.

In actual practice all these adjustments are made before the quantitative tests by using the gas from reserve volumes for setting up purposes. In this way almost instantaneous intensity readings may subsequently be made.

The intensity of emission from 100% Ar or CO_2 is made to correspond to the 100% reading of the transmittance scale on the instrument. This scale is then used to measure the emission intensity of calibration mixtures or test mixtures relative to the intensity of 100% Ar or CO_2 (as the case may be) in terms of % transmittance.

The internal standard method[5] of quantitative spectroscopy requires the presence of an element at fixed concentration in the test sample. In view of the difficulty of fulfilling this condition, the following method of analysis has been developed in the present case.

An internal standard of variable concentration was used. Thus, in the determination of Ar and CO_2, the ratios of peak intensities of the Ar line at λ 2942·9 Å and of the CO_2^+ bandhead at λ 2896 Å were found to be a linear function of their concentrations using 100% Ar or CO_2 (as the case may be) as a check. The values of intensity ratios expressed as log T_{CO_2}/T_{Ar}, were plotted as a function of the concentration ratios expressed as log $[CO_2]/[Ar]$. The term T denotes transmittance. As the values of the ratios cover a wide range, a logarithmic plot of these values spreads them more widely and also improves linearity of the calibration curve. It may be noted that equal absolute errors in log T_{CO_2}/T_{Ar} in different parts of the graph correspond to equal relative errors in concentrations; it is therefore an advantage to use this form of graph because it is desirable to maintain a uniform relative accuracy.

It takes less than 1 min to carry out the final determination.

Table I gives the experimental results which have been used to draw the calibration curve in Fig. 4. The calibration curve is nearly linear from approximately 90% Ar, 10% CO_2 to 9% Ar,

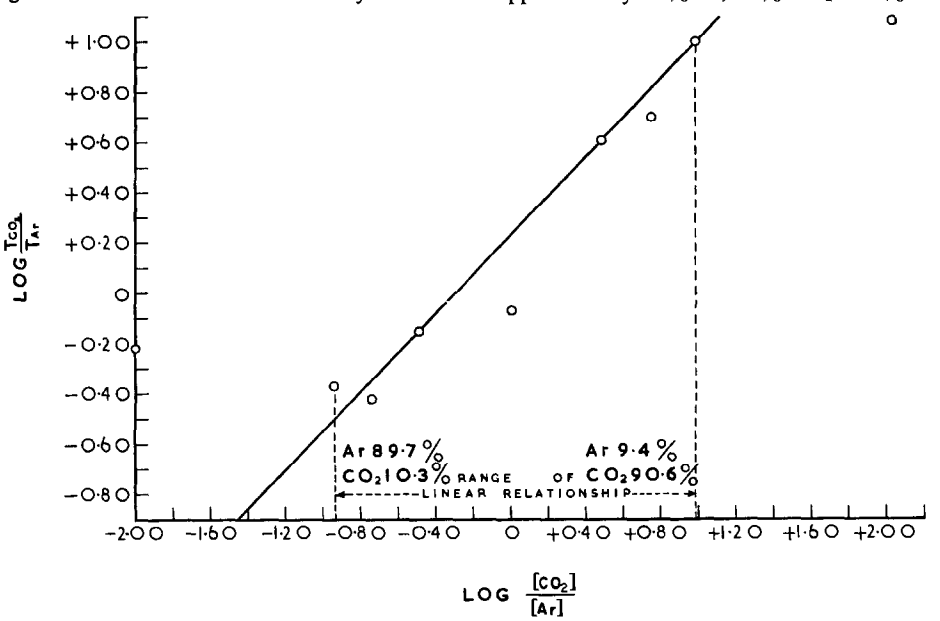


FIG. 4.—Calibration curve
Ar λ 2942·9 Å CO_2 λ 2896 Å
Slits, 0·50 mm Pressure, 0·50 mm of Hg.

91% CO_2. The curve deviates markedly from linearity outside this range. Such departure from linearity at low and high concentrations is the result of two opposing, but unequal factors—a

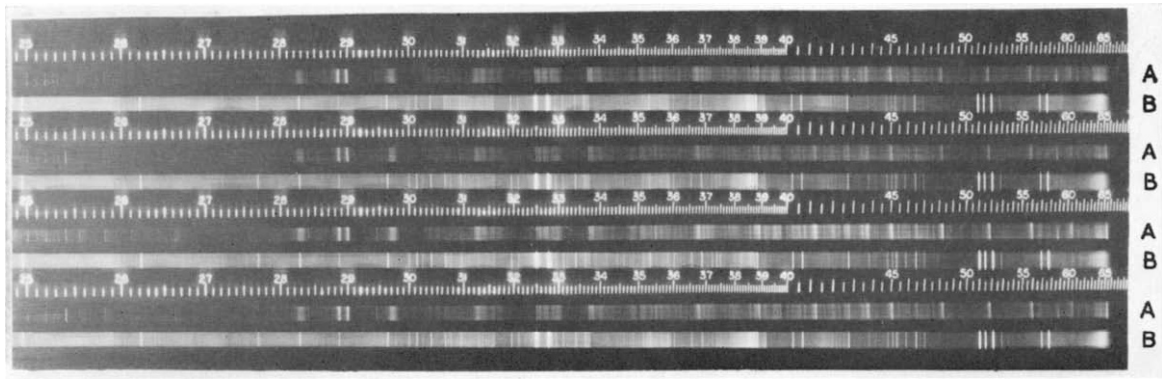


FIG. 3.—Spectra.
A Mixture of Ar, 15% and CO_2, 85%
B Copper arc

background effect which predominates at low concentrations and a self-absorption effect which predominates at high concentrations. Background has the effect of raising and self-absorption of lowering the apparent concentrations. The values of % T in Table I represent the arithmetical mean of two readings taken consecutively.

TABLE I. RESULTS

Serial number	Percentage composition of samples			Percentage transmittance		
	Ar	CO_2	$\log \frac{[CO_2]}{[Ar]}$	T_{Ar} λ 2942.9 Å	T_{CO_2} λ 2896 Å	$\log \frac{T_{CO_2}}{T_{Ar}}$
1	0·9	99·1	+2·04	2·2	26·9	+1·09
2	9·4	90·6	+0·98	1·1	11·0	+1·00
3	15·0	85·0	+0·75	16·0	80·9	+0·70
4	24·3	75·7	+0·49	17·7	71·6	+0·61
5	49·5	50·5	+0·01	25·5	21·9	−0·07
6	75·6	24·4	−0·49	54·8	38·5	−0·15
7	84·6	15·4	−0·74	53·0	20·2	−0·42
8	89·7	10·3	−0·94	61·3	25·9	−0·37
9	99·0	1.0	−2·00	27·6	16·6	−0·22

Reproducibility and accuracy

Reproducibility has been evaluated by using a synthetic standard and running a series of six samples with the same composition under identical operating conditions, with determinations spread over a period of 1 week. The results are shown in Table II. The values of T_{Ar} and T_{CO_2} represent single readings. The reproducibility, expressed as the standard deviation of six tests, is ±3·2% absolute.

For the evaluation of accuracy, it is necessary to run a series of determinations on a number of samples of accurately known composition using the calibration curve. The accuracy is limited by the uncertainty in the exact values of the concentrations in the synthetic standards and the calibration

TABLE II.—REPRODUCIBILITY

Synthetic standard containing Ar 24.3%, CO_2 75.7%

Serial number	Percentage transmittance		$\log \frac{T_{CO_2}}{T_{Ar}}$	Ar found, %	Mean Ar found, %	CO_2 found, %	Mean CO_2 found, %	Deviation, %	Standard deviation, $\sqrt{\frac{\Sigma x^2}{n-1}}$ %
	T_{Ar} λ 2942·9 Å	T_{CO_2} λ 2896 Å							
1	15·1	61·7	0·61	24·4		75·6		2·7	
2	17·8	70·8	0·60	25·3		74·7		3·6	
3	13·5	60·3	0·65	22·8		77·2		1·1	
4	11·0	60·3	0·74	18·6		81·4		3·1	
5	15·5	72·4	0·67	22·0		78·0		0·3	
6	11·2	67·6	0·78	17·3		82·7		4·4	
					21·7		78·3		± 3·2

mixtures. Therefore, for the evaluation of accuracy, the running of synthetic standards with composition calculated from the added components and not determined independently, would accomplish nothing more than the confirmation of the validity of the calibration curve by means of samples, the composition of which are known no more accurately than those of the calibration mixtures. Because of the difficulties of obtaining gas mixtures of accurately known contents, it has not been possible to establish a general level of accuracy.

DISCUSSION

As a result of the dissociation of carbon dioxide into carbon monoxide by the running of the discharge, the apparent values for carbon dioxide change with the time of running of the discharge. Therefore, the time-lag between the beginning of the discharge and the time of taking measurement is most critical. This effect is reduced by

measuring the intensities immediately on switching on the discharge and keeping any unavoidable time-lag constant for all measurements. Satisfactory results are obtained only if this is strictly adhered to and if all other operating conditions are rigidly standardised.

Because of the "clean-up" in the electrical discharge, the intensities of emissions vary with the time of running the discharge.[6] The effect of "clean-up" in electrical discharge is to change the apparent proportions of the gases in a sample. This effect could probably be eliminated by substituting a continuously flowing gas system for the sealed-off gas system; this would ensure the feeding of fresh sample into the discharge cell at constant speed. This, however, could not be attempted with the facilities available in the present work.

The effect of all these factors has been to some extent nullified by using intensity ratios, in which the ratios of the intensities of two variable components, and not their absolute intensities, are related to concentrations. Reproducibility and accuracy may be improved by better instrumentation to ensure constancy of source intensity, and more rigid standardisation of the operating conditions (including gas pressures and the time-lag between the start of discharge and the measurement.)

Prolonged baking of the system and degassing it under high vacuum improve reproducibility and accuracy by removing from the glass surface adsorbed impurities and moisture, the variable concentrations of which may make their effect indeterminate and are, therefore, not amenable to correction.

This technique with the refinement of a flowing gas system and with improvement in instrumentation to ensure constancy in source intensity, might be extended to mixtures of other gases and volatile substances, and might give better reproducibility and accuracy.

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Zusammenfassung—Eine kontinuierliche Entladung bei 230 Megacycl. (erzeugt mittels eines Radiofrequenzhochspannungsgenerators) wurde in einem abgeschlossenen System in Verbindung mit einem Quartzprismenspectrophotometer herangezogen um binäre Mischungen von Argon und Kohlendioxyd zu studieren. Die Konzentrationen in Mischungen von 15–90% Ar und 85–10% CO_2 wurden mit einer Reproduzierbarkeit von $\pm 5{\cdot}8$ (mittlerer Fehler) bestimmt. Die Bestimmung kann in etwa einer Minute durchgeführt werden, was die Methode der spektrographischen Bestimmung überlegen macht. Es ist anzunehmen, dass mit verbesserten Instrumenten, (höhere Konstanz der Erregerquelle und Ersatz des abgeschlossenen System durch einen kontinuierlichen Gasstrom) die Methode auch auf andere Gasmischungen angewendet werden kann; auch sollten dann höhere Genauigkeit und Reproduzierbarkeit erreichbar sein.

Résumé—Les auteurs ont utilisé une décharge continue à 230 mégacycles, produite par un générateur très haute tension à fréquence radio, dans un système gazeux en tube scellé, en liaison avec un spectrophotomètre à prisme de quartz pour étudier des mélanges binaires d'argon et d'anhydride carbonique. Les concentrations du mélange dans le domaine 15 à 90% d'argon, 85 à 10% d'anhydride carbonique ont été dosées avec une reproductibilité de $\pm 5{,}8$, exprimée en déviation standard. Les dosages peuvent être réalisés en une minute environ, ce qui rend cette technique supérieure à la spectrographie. La méthode

mise au point laisse penser que, avec un appareillage amélioré assurant la constance de l'intensité de la source et la substitution d'un gaz s'écoulant continument au système en tube scellé, il serait possible d'étendre cette technique à des mélanges d'autres gaz et d'obtenir une reproductibilité et une précision meilleure.

REFERENCES

[1] C. L. Chakrabarti, R. J, Magee and C. L. Wilson, *Talanta*, 1962, **9**, 43.
[2] T. Given, R. J. Magee and C. L. Wilson, *ibid.*, 1959, **3**, 191.
[3] R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra.* Chapman and Hall, Ltd., London, 1950.
[4] C. S. White, L. C. Watkins, Jr. and E. E. Fletcher, *J. Aviation Medicine*, 1956, **27**, 332; C. S. White *Aviation Medicine Selected Reviews*, Avardograph No. 25. 1958 p. 157.
[5] W. Gerlach, *Z. anorg. Chem.*, 1925 **142**, 383; W. Gerlach and E. Schweitzer, *Foundations and Methods of Chemical Analysis by the Emission Spectrum*, Adam Hilger, Ltd. London, 1931.
[6] R. A. Wolfe and O. S. Duffendack, *Proceedings of the Sixth Summer Conference on Spectroscopy and its Application.* Massachusetts Institute of Technology, 1939, p. 66.

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UNTERSUCHUNG DER KATIONENSORPTION AUS KOMPLEXANMEDIUM—III*

CHROMATOGRAPHISCHE TRENNUNG VON STRONTIUM UND BARIUM

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Zusammenfassung—Es wurde eine neue Methode zur Trennung von Strontium und Barium unter Anwendung der Ionenaustauschchromatographie ausgearbeitet. Barium- und Strontiumionen werden an einem stark sauren Kationenaustauscher (Amberlit IR 120 in NH_4^+-Cyclus) adsorbiert, wonach Strontium mit 0,02–0,05 m DCyTE in 0,4 m Ammoniumacetat (pH 6,3–7,2) ausgewaschen wird. Im Eluat ermittelt man den Strontiumgehalt flammenphotometrisch. Bei der gleichzeitigen Bestimmung von Calcium und Strontium neben überschüssigem Barium, wäscht man Calcium mit dem gleichen Elutionsmittel bei pH 5,1 aus. Die neu vorgeschlagene Methode wurde zur Bestimmung von Strontium und Calcium in Bariummineralen, insbesondere in Schwerspat und Witherit angewendet.

DIE Untersuchung der Sorption von Erdalkalimetallen aus Lösung von ÄDTE bzw. 1,2-Diaminocyclohexan-*N*-*N*,*N*′,*N*′-tetraessigsäure (DCyTE) an Ionenaustauschern[1] ergab, dass insbesondere die DCyTE ein geeignetes chromatographisches Reagens zur vollständigen Trennung von Calcium und Strontium[2] darstellt. In der vorliegenden Arbeit wird gezeigt, dass sich dieses Reagenz auch zur analogen Trennung von kleinen Mengen Strontium von überschüssigem Barium eignet und zur quantitativen Bestimmung von Strontium in Schwerspat and anderen Bariummineralen mit Erfolg angewendet werden kann.

APPARATE UND REAGENZIEN

Die Standardlösungen von Strontium und Barium wurden aus p.a. Präparaten der Fa. E. Merck, Darmstadt, DBR, bzw. der Fa. Johnson and Matthey, England, hergestellt. Als Pufferlösung wurde 1 m Ammoniumacetat verwendet, dessen pH auf den erwünschten Wert mit verdüntem Ammoniak eingestellt wurde. Ein weiterer Puffer war Triäthanolamin und sein Hydrochlorid, das sich insbesondere für den pH-Bereich von 7,2 aufwärts bewährte. Die Herstellung der Komplexbildner bzw. ihrer Lösungen und die Beschreibung der verwendeten Apparate wurden bereits in den vorangehenden Arbeiten dieser Reihe[2] behandelt.

ERGEBNISSE

Aus der gegenseitigen Lage der Sorptionskurven von Strontium und Barium aus DCyTE-Medium ist ersichtlich, dass es keinen pH-Wert, bzw. pH-Bereich gibt, in dem eines der beiden untersuchten Erdalkalimetalle als undissoziierter DCyTE-Komplex vorliegt, während die andere analoge Komplexverbindung des zweiten Metalls als vollständig dissoziiert zugegen ist. Aus diesen Grunde ist es unmöglich, die Trennung des Strontiums von Barium durch Aufguss aus DCyTE-Medium durchzuführen. Hierzu muss man sich der Ionenaustauschchromatographie bei geeignetem pH-Wert

* II. Mitteilung: *Talanta*, 1961, **8**, 705.

bedienen. Es wurde festgestellt, dass beim Durchgang des Komplexbildners durch die Säule das sorbierte Strontium auch bei einem solchen pH-Wert ausgewaschen wird, bei dem die Barium-Komplexbildung praktisch ausbleibt. Es war daher nötig, eine Waschlösung mit einem solchen pH-Wert zu finden, bei dem das Auswaschen des Strontiums mit hinreichender Geschwindigkeit vor sich geht und das Barium zugleich noch nicht eluiert wird. Zu diesem Zweck wurde zunächst die Trennung des Strontiums und Bariums in Abhängigkeit vom pH-Wert des Elutionsmittels verfolgt. Die beiden zu bestimmenden Metalle (5,2 mg Sr und 300 mg Ba) wurden an die Katexsäule aus einem Volumen von 80 ml adsorbiert, nach dem Auswaschen der Säule mit Wasser wurden die Metalle mit 0,02 m DCyTE in 0,4 m Ammoniumacetat, dessen pH-Wert entsprechend eingestellt wurde, direkt in einem 100 ml Messkolben eluiert. In dieser Lösung wurden Strontium flammenphotometrisch und Barium spektralanalytisch[3] bestimmt.

Aus den so gewonnenen und in Tab. I. zusammengefassten Ergebnissen geht hervor, dass es in dieser Weise möglich ist Strontium von überschüssigem Barium

TAB. I. pH ABHÄNGIGKEIT DER CHROMATOGRAPHISCHEN TRENNUNG VON STRONTIUM UND BARIUM
Elution mit 0,02 m DCyTE im 0,4 m Ammoniumacetat.
Sr = 5,2 mg; Ba = 300,0 mg.

pH der Elutionslösung		Sr gefunden %	Ba in der Strontium-fraction, % aus der gesamten Barium-menge
Anfangswert	Endwert nach der Elution		
6,3	6,2	99,5	0,05
6,6	6,45	99,2	0,05
7,0	6,75	99,0	0,05
7,3*	7,3	99,3	0,05
7,4	70,5	99,2	0,05
7,8	7,60	99,0	0,20
8,45	8,20	99,0	12,50

* 0.25 m Triäthanolamin HCl auf pH 7,3 gebracht.

innerhalb des pH-Bereiches von 6,3–7,8 verlässlich abzutrennen. Unter diesen Bedingungen sind die Bariummengen in der Strontiumfraktion kleiner als 0,05% des ursprünglichen Bariumgehaltes. Es ist daher möglich, das in der Säule zurückgehaltene Barium mit einem geeigneten Reagenz auszuwaschen und mittels einer passenden analytischen Methode zu bestimmen. Den optimalen pH-Bereich realisiert man entweder mit Hilfe von mit Ammoniak eingestelltem Ammoniumacetat, oder mit 0,25 m Triäthanolamin, dessen pH-Wert man mit Salzsäure auf den Wert von 7,0–7,5 einstellt.

Wegen des ziemlich geringen Puffervermögens der Ammoniumacetat-Lösung kommt es beim Auswaschen des Strontiums d.h. bei der Bildung des Sr-DCyTE-Komplexes, infolge des Freiwerdens von Wasserstoffionen zu einer geringen pH-Änderung (s. Tab. I), die jedoch auf die Vollständigkeit des Auswaschens des Strontiums beim angegebenen Volumen des Elutionsmittels ohne Einfluss ist. Ferner wurde festgestellt, dass die flammenphotometrische Bestimmung von Strontium aus komplexbildendem Medium im angegebenen pH-Bereich durch pH-Änderung nicht beeinflusst wird.

Auf Grund dieser Ergebnisse wurde zur quantitativen Trennung des Strontiums von überschüssigem Barium die nachfolgende Vorschrift ausgearbeitet:

Eine in 80 ml etwa 0,5–10 mg Strontium und bis 300 mg Barium enthaltende Lösung wird mit einer Durchlaufgeschwindigkeit von 2 ml min^{-1} . cm^{-2} an der Katexsäule adsorbiert und die Säule wird mit 30–50 ml Wasser ausgewaschen. Dann wäscht man die Säule mit 20–40 m 0,4 m Ammoniumacetat von pH-Wert 7,2 bis zum konstant bleibenden pH-Wert der ausfliessenden Lösung aus. Hierauf eluiert man das Strontium mit 100 ml 0,02–0,03 m DCyTE in 0,4 m Ammoniumacetat von pH 7,2 aus. Das Eluat sammelt man in einem 100 ml Messkolben und bestimmt das Strontium flammenphotometrisch. Die Auswertung geschieht mit Hilfe einer Eichkurve die man an Hand von Strontium-Standardlösungen, die die gleichen Mengen DCyTE und Pufferlösung wie die zu analysierende Probe enthalten, herstellt. Einige Ergebnisse der Trennung von synthetischen, Barium und Strontium enthaltenden Gemischen sind in Tab. II wiedergegeben. Aus der gleichen Tabelle entnimmt man, dass auch beim Verhältnis Sr:Ba 1:300 die Fehler der Bestimmung kleiner als 1 % sind.

DER EINFLUSS VON BEGLEITELEMENTEN

Die beschriebene Trennung von Strontium und Barium war vor allem auf die Analyse von Schwerspat, Witherit und einigen bariumhaltigen Silikaten gezielt. Daher wurde auch der Einfluss der in den obigen Mineralen vorkommenden Begleitelemente untersucht.

TAB. II. BESTIMMUNG VON STRONTIUM NEBEN ÜBERSCHÜSSIGEM BARIUM
Elution mit 0,03 m DCyTE im 0,4 m Ammoniumacetat
Ba = 300 mg; pH = 7,2

Sr, *mg*		Differenz, %
gegeben	gefunden	
10,40	10,38	−0,19
8,32	8,24	−0.94
7,28	7,26	−0,28
6,24	6,24	±0,00
5,20	5,20	±0,00
4,16	4,16	±0,00
2,08	2,09	+0,48
1,04	1,04	±0,00

Die eigentliche Sorption und chromatographische Trennung der beiden Elemente wird durch zu hohe, beim Sodaaufschluss in den Analysengang eingetragene Mengen von Natriumionen gestört. Die entstandenen Erdalkalicarbonate enthalten nach mehrmaligem Auswaschen mit Ammoniumcarbonat nur wenig Natrium, das die Strontiumbestimmung nicht beeinflusst. Diese kleinen Natrium mengen wirken sich jedoch auf die eventuelle Calciumbestimmung störend aus. In einem solchen Fall muss man die Erdalkalicarbonate in verdünnter Säure lösen und nochmals mit Ammoniumcarbonat fällen.

Falls die Probe neben Strontium und Barium auch Calcium enthält, trennt man zunächst chromatographisch das Calcium mit 0,02–0,05 m DCyTE in 0,4 m Ammoniumacetat von pH 5,1 ab. Da das Calcium in den erwähnten Mineralen nur in Mengen von unterhalb 1 % vorkommt, genügen zu seiner quantitativen Abtrennung 100 ml dieser Lösung. Den Calciumgehalt kann man unmittelbar aus dem Eluat flammenphotometrisch bestimmen. Gleichzeitig mit Calcium wird auch Magnesium eluiert.

Die am Kationenaustauscher adsorbierten Eisen(III)-ionen werden unter den beschriebenen Bedingungen wahrscheinlich infolge der langsamen Bildung des Hydroxokomplexes nur zum Teil eluiert, jedoch wird die nachfolgende flammenphotometrische Strontiumbestimmung mit diesen Eisenmengen (1 % Sr neben 7 % Fe) nicht

gestört. Bei grösseren Eisen- und besonders Aluminiummengen ist es vorteilhaft, die dreiwertigen Metalle durch Sorption aus Citratpuffermedium (pH 3 bis 3,5) abzutrnnen[4]. In diesem Medium bilden die drei, bzw. vierwertigen Metalle anionische Citratkomplexe, die am Ionenaustauscher nicht adsorbiert werden.

PRAKTISCHE ANWENDUNG

Etwa 0,5 g fein zerriebenes Mineral schliesst man etwa 20–30 min. lang mit 3 g wasserfreier Soda auf, kühlt ab und lässt die Schmelze in warmem Wasser gut zerfallen. Die abgeschiedenen Carbonate und Hydroxyde sammelt man auf dem Filter und wäscht sie 5-mal mit 1% igem Ammoniumcarbonat aus. Hierauf löst man den Niederschlag in möglichst wenig verdünnter Salzsäure. Aus der vorwiegend Erdalkalimetalle enthaltenden Lösung entfernt man die Säure durch Abdampfen auf kleines Volumen, macht dann mit verdünntem Ammoniak alkalisch und fällt in der Wärme mit 20–30 ml 10% igem Ammoniumcarbonat die Erdalkalien.

Variante A: Analyse von mineralogisch separierten Schwerspatsorten: den durch Filtrieren abgetrennten Niederschlag löst man in möglichst wenig Salzsäure, verdünnt auf 80–100 ml und lässt die Lösung durch die Katexsäule mit der bereits erwähnten Durchlaufgeschwindigkeit fliessen. Zuletzt wäscht man die Säule mit 50 ml Wasser aus.

VarianteB: Für technische Schwerspatsorten und Bariumalumosilikate: den Carbonatniederschlag löst man in Salzsäure, dampft zur Trockne ab und entfernt in üblicher Weise die Kieselsäurereste. Alsdann versetzt man die Lösung mit 1 g Citronensäure und stellt den pH unter potentiometrischer

TAB. III. DIE STRONTIUMBESTIMMUNG IN NATÜRLICHEN SCHWERSPATEN

Probe	Sr gefunden, %	Sr durch Kontrollmethoden bestimmt, %	Bemerkung
I	0,91[6]	0,89[a] 0,93[b]	Durchschnitt aus 11 Bestimmungen; Standartabweichung $\sigma = \pm 0{,}85\%$
II	0,60 0,59[c]	0,65[a]	Durchschnitt aus 6 Bestimmungen
III	0,77	0,80[a]	Durchschnitt aus 3 Bestimmungen

[a] spektralanalytisch. [b] chemisch. [c] Eisen als Citratkomplex abgetrennt.
Bei der Probe Nr. I wurde der Calciumgehalt nach der beschriebenen Methode 0,11% bestimmt, spektralanalytisch 0,10% gefunden.

Kontrolle auf den Wert von 3–3,5 ein. Hierauf sorbiert man die Erdalkalien bei einer Durchlaufgeschwindigkeit von 1,5–2 ml. min^{-1}. cm^{-2} und wäscht zum Schlusse die Säule mit 50 ml Wasser aus.

Bestimmung von Calcium: Die Säule wäscht man mit 0,4 m Acetatpuffer von pH 5,1 aus bis das Eluat den gleichen pH-Wert aufweist. Das sorbierte Calcium eluiert man mit 100 ml 0,02-0,05 m DCyTE in 0,4 m Ammoniumacetat von pH 5,1 aus. Das Eluat fängt man in einen 100 ml Messkolben auf und bestimmt den Calciumgehalt flammenphotometrisch. Die Auswertung des Calciumgehaltes geschieht mit Hilfe einer Eichkurve, die man an Hand von Calciumstandardlösungen, die sowohl das Komplexan als auch die Pufferlösung enthalten, hergestellt hat.

Bestimmung von Strontium: Die Kolonne wäscht man mit 30 ml Wasser und mit 0,4 m Ammoniumacetat von pH 7,2 aus. Das sorbierte Strontium eluiert man dann mit 100 ml 0,02 m DCyTE in 0,4 m Ammoniumacetat des gleichen pH-Wertes. Das Eluat wird wiederum in einen 100 ml Messkolben aufgefangen und das Strontium wird photometrisch nach der bereits erwähnten Weise bestimmt. Die Durchlaufgeschwindigkeit beträgt sowohl bei der Calciumbestimmung als auch bei der Strontiumbestimmung 1–1,5 ml. min^{-1}. cm^{-2}.

Das am Ionenaustauscher zurückgehaltene Barium kann man entweder mit ammoniakalischer ÄDTE vom pH 10 oder mit 3 m HCl auswaschen und seine Bestimmung im Eluat am besten komplexometrisch[5] durchführen.

Die obige Strontiumbestimmung in Schwerspat wurde durch Analyse von synthetischen Gemischen und durch wiederholte Analyse von 3 natürlichen Schwerspatsorten beglaubigt. Die Probe Nr. 1 war ein separiertes sehr reines und nur Spuren von Verunreinigungen enthaltendes Mineral, die Probe Nr. 2 enthielt 15% Siderit. Die Probe Nr. 3 war ein 5% Fluorit enthaltender Schwerspat. Die in Tab. III zusammengefassten Ergebnisse zeigen, dass die Methode gut reproduzierbare, mit den Ergebnissen der Spektralanalyse und mit dem deklarierten Gehalt übereinstimmende Werte liefert. Ihr Vorteil gegenüber den bisher zu diesem Zweck verwendeten Methoden ist vor allen Dingen in der Einfachkeit und Schnelligkeit der praktischen Ausführung zu sehen.

Wenn es sich nur um die schnelle Strontiumbestimmung handelt, so kann man die obenbeschriebene Ammoniumcarbonatfällung auslassen. Die durch den Sodaaufschluss entstandenen Carbonate können direkt nach Auswaschen und Auflösung (in verdünnter Salzsäure) an dem Kationenaustauscher sorbiert werden.

Es ist den Autoren eine angenehme Pflicht der Fa. J. R. Geigy, Basel, Schweiz, für die freundliche Überlassung einer grösseren Menge 1,2-Diaminocyclohexan-N,N,N′,N′-tetraessigsäure ihren Dank auszusprechen.

Übersetzt von A. Emr, Prag.

Summary—A new method, using ion-exchange chromatography, has been developed for the separation of strontium and barium. The ions are adsorbed on a strong acid exchanger (Amberlite IR 120 in the ammonium form). Strontium is eluted with 0·02–0·05*M* 1,2-diaminocyclohexane-*N,N,N′,N′*-tetra-acetic acid (DCyTA) in 0·4*M* ammonium acetate (pH 6·3–7·2), and is determined in the eluate by flame-photometry. For the simultaneous determination of calcium and strontium in the presence of excess barium, the calcium is removed by the same eluent at pH 5·1. This method has been applied to the determination of strontium and calcium in barium minerals such as barytes and witherite.

Résumé—Les auteurs ont mis au point une nouvelle méthode de chromatographie d'échange d'ions pour la séparation du strontium et du baryum. Les ions sont adsorbés sur un échangeur acide fort (Amberlite IR 120 sous forme ammonium)· Le strontium est élué par de l'acide 1,2 diaminocyclohexane N,N,N′,N′-tétracétique (DCyTA) 0,20–0,05 M dans l'acétate d'ammonium 0,4 M (pH 6,3–7,2) et est dosé dans l'éluat par photométrie de flamme. Pour le dosage simultané du calcium et du strontium en présence d'un excès de baryum, le calcium est éliminé par le même éluant à pH 5,1. Cette méthode a été appliquée au dosage du strontium et du calcium dans des minerais de baryum comme les barytes et la withérite.

LITERATUR

[1] P. Povondra, R. Přibil und Z. Šulcek, *Talanta*, 1960, **5**, 86.
[2] P. Povondra, Z. Šulcek, R. Přibil und R. Štangl, *ibid.*, 1961, **8**, 705.
[3] I. Rubešca und M. Mikšovský, *Věstník ÚÚG*, 1961, im Druck.
[4] P. Povondra und Z. Šulcek, *Coll. Czech. Chem. Comm.*, 1959, **24**, 2398.
[5] C. N. Reilley, R. W. Schmid und D. W. Lamson, *Analyt. Chem.*, 1958, **30**, 953.

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CHEMILUMINESCENCE OF LUMINOL AND HAEMIN

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Summary—A study of the luminescence of haemin-luminol mixtures has shown that haemin is a chemiluminescent material, and a mechanism is proposed for the haemin-luminol reaction. The course of the reaction depends on the relative concentrations of the components and the alkalinity of the solution.

THE brilliant chemiluminescence emitted by luminol (3-aminophthalhydrazide) on oxidation in an alkaline medium is well known and this phenomenon has been studied for many years. The chemiluminescence shown by phthalhydrazide derivatives when oxidised by sodium hypochlorite was studied by Zellner and Dougherty[1] in 1937, and a series of studies on the luminescence of luminol has been published by Weber and coworkers.[2–10] The latter series was mainly concerned with the effect of different catalysts and inhibitors on the intensity of light emitted by luminol when oxidised by hydrogen peroxide. The behaviour of luminol in the presence of potassium hexacyanoferrate(III) as catalyst has also been studied.[11,12]

Luminol was introduced as a chemiluminescent indicator for the titration of acids by bases by Kenny and Kurtz;[13] and Erdey and his coworkers[14,15] have used this reagent as a chemiluminescent indicator in a variety of redox titrations. Luminol is not a satisfactory indicator for the titration of bases by acids because the indicator is irreversibly oxidised in an alkaline medium in the presence of the catalysts normally used to increase the intensity of luminescence, *e.g.* haemin. However, it has recently been observed[17] that a mixture of fluorescein and luminol may be used as a reversible chemiluminescent indicator for acid-base titrations provided that the temperature of the solution is 60° at the beginning of the titration.

Attempts have since been made to eliminate the need for an elevated temperature by adding a small amount of catalyst. This aim has not been achieved but subsequent studies on the luminol-haemin system have nevertheless provided some interesting results which, it is felt, are worth reporting and discussing.

EXPERIMENTAL

To alkaline solutions (0·001*N* to 1*N* sodium hydroxide) containing 1 ml of 6% hydrogen peroxide were added 1 or 2 ml of luminol solution ($5{\cdot}7 \times 10^{-4}M$). These mixtures were then added to varying volumes of haemin solution ($1{\cdot}3 \times 10^{-5}$ *M*) and mixed thoroughly. The volume of alkali present was adjusted to give a total volume of 10 ml after mixing. The mixing was carried out in a dark room, and both the duration of the chemiluminescence and its relative intensity were measured.

In some tests haemin was replaced by sucrose, glycerol or glucose (1-g quantities) in warm solution, and in other tests the luminol was eliminated.

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RESULTS

The results of all of these comparative tests may be summarised as follows:

(1) The rate of fading of the normal blue chemiluminescence was slowest in approximately 0·01*N* sodium hydroxide solution. The rate was just slightly faster in more dilute solutions but fading was extremely fast in 0·1*N* and 1*N* sodium hydroxide solutions.

(2) For a given concentration of luminol in 0·01*N* sodium hydroxide, the intensity of the light emitted increased with the amount of haemin added, although the colour persisted for longer periods with smaller additions of haemin.

(3) In alkalinities of 0·01*N* and less, the chemiluminescence ceased because of the loss of the catalytic effect of the haemin present. The addition of further haemin to such solutions resulted in the return of blue luminescence.

(4) In alkalinities of 0·1*N* or greater, the luminol was destroyed in the luminescent reaction. Luminescence was restored by adding more luminol.

(5) The rate of the initial reaction varied with the concentration of haemin at the time of mixing.

(6) After the original blue light had faded from solutions of alkalinity less than 0·02*N*, a pale yellowish-green light was observed. In many cases the light could be observed as bright specks on suspended particles in the solution; these slowly collected at the bottom of the vessel.

(7) Warm (60°) alkaline solutions of haemin oxidised by hydrogen peroxide emitted weak greenish chemiluminescence of very short duration. The duration of this chemiluminescence was increased by adding glycerol to the original solution.

(8) The intensity of the pale blue luminescence obtained by oxidising alkaline solutions of luminol with hydrogen peroxide (without catalysts) increased with temperature. The intensity was further enhanced if sucrose, glucose or glycerol was present during the heating. On cooling the luminescence faded, but the rate of fading was slower in the presence of the carbohydrates.

(9) Provided that the acid solutions are initially heated to 60°, a mixture of 1 ml of 1% luminol and 1 ml of glycerol is a suitable chemiluminescent indicator for the titration of acids by bases. When hot base solution is titrated by acid the results are low, because of the formation of acid through oxidation of the glycerol. The error is lessened by adding the glycerol to the hot alkali just before titration.

DISCUSSION

The first three of the above findings are in agreement with the conclusions of Weber, Rezek and Vouk.[3] These workers measured the intensity of the luminescence of luminol under different conditions using a photoelectric circuit. The concentration of luminol used by Weber and his coworkers was about ten times greater than that used in the present investigation, but comparable concentrations of haemin were used in both cases. In the haemin-catalysed reaction, the maximum brilliance was obtained with concentrations of sodium hydroxide between 0·025*N* and 0·05*N*, and the maximum half-life was obtained in 0·015*N* sodium hydroxide solution. At low concentrations of catalyst, the maximum intensity was found to vary with the concentration of catalyst. With alkalinites up to 0·04*N* sodium hydroxide, all of the catalyst was altered irreversibly in the course of the reaction and the other components (hydrogen peroxide and luminol) were probably partially but by no means

completely destroyed in the reaction. For example, the addition of fresh catalyst to a number of samples 7 min after the initial luminescence reaction resulted in further bright luminescence, the intensity of this second emission being about 75% of the intensity of the original emission.

Using sodium hypochlorite as the oxidising agent, Zellner and Dougherty[1] observed a maximum emission intensity in 0·015*N* sodium hydroxide solutions. The intensity of luminescence decreased with increasing alkalinity, being reduced to about one-tenth of the maximum intensity in 0·5*N* sodium hydroxide solution.

The rate of oxidation of luminol by sodium hypochlorite was followed by measuring the volume of nitrogen liberated. This was found to accelerate markedly with hydroxyl ion concentration, *e.g.* the time required for half of the total nitrogen gas to be evolved was 4·9 min in 0·17*N* sodium hydroxide, 2·8 min in 0·33*N* sodium hydroxide and 0·9 min in 0·5*N* sodium hydroxide.

The evidence of accelerated destructive oxidation with increasing alkalinity gives an explanation for the fourth observation in this current study, namely, the destruction of luminol in the luminescent reactions using alkalinities greater than 0·1*N*.

The hydroxyl ion concentration of the test solution can influence the luminescence reaction in a number of ways. Weber[2,3] has shown that the carbonyl form of luminol is required for the oxidation of luminol. At pH 8 about 5% of luminol is present in this form, and the transformation is complete at pH 12·6. When hydrogen peroxide is present, the concentration of the ion ($H_2O_2 \cdot OOH^-$) also reaches a maximum concentration at about the same pH.[18] Hence the maximum intensity of luminescence observed in solutions having an alkalinity of about 0·02*N* sodium hydroxide may perhaps be attributed in a large part to the presence in maximum possible concentration of these two reacting species.

The composition of the catalyst, haemin, can also vary with the alkalinity of the solution. In the presence of excess alkali, haemin (ferri-proto-porphyrin) forms a bivalent anion of ferri-proto-porphyrin hydroxide in which two carboxyl groups of the propionic acid side chains are ionised and the iron is bound to the hydroxyl group of the base and to one mole of water as well as to the four nitrogen atoms in the haemin molecule.[19] The existence of this hydroxide complex explains the suspended particles noted in observation (6) where such particles appeared as a source of yellow-green chemiluminescence.

Weber[6] has related the catalytic effects of iron complexes such as haemin to the behaviour of the co-ordination valencies not bound to the nitrogen of the original molecule. Thus, with haemin, both the fifth and sixth valences of the iron^{III} may be catalytically active. At the same time, replacement of the water from these co-ordination sites by more strongly bound ligands (*e.g.* CN^-, OH^-) inhibits the catalytic effect. Weber considers that the catalyst can exhibit two kinds of oxidation action: (a) as a peroxidase, and (b) as a catalase. In the first case, one mole of hydrogen peroxide acts on the substrate to form luminol peroxide, which then forms an intermediate addition complex with the catalyst. This complex quickly decomposes in the presence of water to give an oxidation product of luminol, free catalyst and hydroxyl ions. In the second case, the luminol peroxide is in turn oxidised by another mole of hydrogen peroxide, resulting in the formation of the same oxidised species of luminol as before, a higher concentration of hydroxyl ions and the liberation of atomic oxygen with dehydration of the substrate. In the formation of the peroxide

catalyst complex, the O of the luminol peroxide is bound to the free (sixth) co-ordination valence of the iron^{III} in the catalyst.

The formation of an intermediate addition complex has also been postulated by the present authors[17] to explain the behaviour of the luminol-fluorescein system. The observation made in this present study, that haemin is a chemiluminescent material, would indicate a substantial similarity between the two systems. When oxidised separately in alkaline solutions, haemin and fluorescein both chemiluminesce very weakly and require further excitation by heat.[16] Luminol alone is also a weak emitter unless heated. However, a mixture of luminol with either of the other two compounds emits brilliant luminescence. When fluorescein is the additive the emitted light is green, and with haemin the emitted light is bright blue.

All three compounds are known to form oxygen complexes and it has been suggested that removal of the bound oxygen can leave a molecule in an excited triplet state. Reversion of the molecule to a singlet state may then result in the release of the excess energy in the form of light.[25] The formation of oxygen complexes has been stated to favour singlet-triplet transformation; and the existence of a triplet state with haemin has been proved.[23]

The stable complex formed between haemin and hydrogen peroxide has been examined, and has been found to contain one mole of haemin and two moles of hydrogen peroxide.[20] A polarographic study led to the conclusion that only undissociated hydrogen peroxide molecules take part in the reaction and combine with the haemin.[21] On the other hand, the action of haemin in speeding up the evolution of oxygen from hydrogen peroxide has been analysed and discussed on the basis of three reactions:

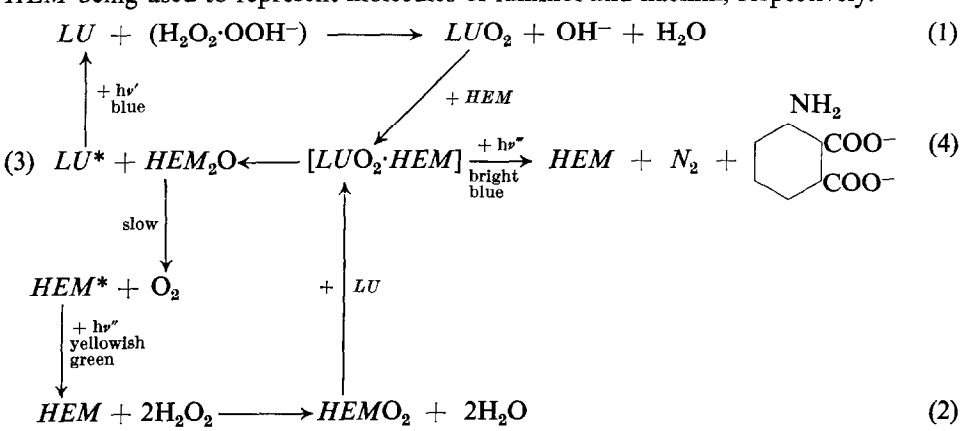
$$\text{(a)}\ \text{Cat.} + H_2O_2 = \text{Cat. O} + H_2O$$

$$\text{(b)}\ \text{Cat.} + 2H_2O_2 = \text{Cat.} \begin{matrix} O \\ O \end{matrix} + 2H_2O$$

$$\text{(c)}\ \text{Cat.} \begin{matrix} O \\ O \end{matrix} = \text{Cat.} + O_2$$

where Cat. is the catalyst. Reactions (a) and (b) were considered to reach rapid equilibrium while reaction (c) was postulated as a slow step.[22]

On the basis of all of this evidence, the following is proposed as the mechanism of the luminol-haemin reactions observed in this latest study, the symbols *LU* and *HEM* being used to represent molecules of luminol and haemin, respectively.



The relative importance of the competing reactions is controlled by the pH of the solution and the concentration of reactants.

Since it has been shown[21] that only undissociated hydrogen peroxide molecules react with haemin, the importance of reaction (2) will increase as the pH of the solution is lowered. On the other hand, since luminol reacts preferably with the ($H_2O_2 \cdot OOH^-$) ion, reaction (1) should reach maximum importance at pH values around 12 to 13. The liberation of nitrogen from oxidised luminol solutions has been observed to be accelerated by increased pH, hence reaction (5) will become increasingly important with increasing hydroxyl concentration in the solution.

In dilute alkaline solutions, *e.g.* $<0{\cdot}01N$ sodium hydroxide, the haemin-luminol reaction can be considered to follow the course of reactions (2) and (3) *or* (1) and (3), the relative importance of each depending on the exact pH. When luminol is present in excess, reaction (1) will be favoured, particularly at pH values of the order of 12 to 13. Increasing the concentration of haemin present will increase the rate of intermediate complex formation and thus increase the initial maximum intensity.

Kobozev[22] postulated that the decomposition of $HEMO_2$ is a slow process, and this slow step can be considered to influence the duration of luminescence. The speckles of greenish-yellow light observed in the solutions after the fading of the blue luminol colour can be attributed to the chemiluminescence of the activated haemin formed on decomposition of the $HEMO_2$. The decomposition product lacks catalytic properties and it may be suggested that both the fifth and sixth co-ordinate valencies of iron are occupied by hydroxyl ions, thus reducing both the solubility and the co-ordinating power of the compound.

Increasing the H_2O_2 content of the reaction mixture will tend to favour reaction (2), thus reducing the amount of haemin available to form an association complex with luminol peroxide. This in turn means less light emission, as has been observed by Weber.[6]

As the alkalinity of the test solutions is increased reaction (4) becomes more important, and light emission is accompanied by an increasing degree of destruction of the luminol. Above pH 12, however, the concentration of ($H_2O_2 \cdot OOH^-$) is reduced, and this reduces the intensity of emission by inhibition of reaction (1). In the absence of free hydrogen peroxide the haemin molecule should remain virtually unchanged and retain its catalytic properties. This is supported by experiment, because the addition of further luminol to extinguished solutions of alkalinity greater than $0{\cdot}1N$ sodium hydroxide results in a return of the bright blue luminescence.

The above mechanism postulates three types of emitted light. The existence and characteristics of that emitted in reaction (4) is well known and requires no further discussion. The yellowish-green light attributed to activated haemin has been observed when haemin is oxidised by hydrogen peroxide in hot alkaline solution, as well as in the mixed indicator study. The greater persistence of this emission in the presence of luminol is analogous to the phenomena observed previously with fluorescein-luminol mixtures. When oxidised alone fluorescein luminesced very weakly, but in the presence of luminol brilliant green light was emitted with little apparent destruction of the luminol. In fact, oxidation of an alkaline mixture of haemin, luminol and fluorescein with hydrogen peroxide yields bright green light, not blue as obtained in the absence of fluorescein.

The third colour is the blue postulated for the deactivation of the luminol species

in reaction (3). The possibility of such an emission is indicated by the behaviour of alkaline peroxide solutions containing luminol when they are heated in the presence of glycerol or sugars. Heating the luminol solution alone causes a marked increase in intensity of a deep blue radiation and this intensity is further increased in the presence of glycerol or sugars. As long as the temperature remains constant, the intensity remains constant and there is no marked destruction of the luminol in the sense of equation (4). On cooling, the intensity decreases (slowly in the presence of the carbohydrates) but it can be restored by further heating.

This behaviour can be explained by conclusions similar to those reached by Parker and Hatchard.[24] These workers used a high-sensitivity spectrophotometer to study the very weak, long-lived emission spectra of eosin in glycerol and ethanol. The visible band of long-lived luminescence was found to be delayed fluorescence produced by thermal agitation of the eosin from the triplet to the excited singlet level. The probabilities of inter-system crossing from the upper singlet to triplet, and from triplet to upper singlet state, were found to be of the same order of magnitude, being greater in glycerol than in the more fluid ethanol.

The luminol-glycerol reaction can thus be ascribed to the formation of the triplet state by thermal decomposition of the luminol peroxide formed during the oxidation process followed by transition of the molecule from the triplet state to an excited singlet level state, the probability of this latter transition being increased by the presence of glycerol. This need for thermal agitation from the triplet to the upper singlet state explains the observation that the intensity of chemiluminescence of uncatalysed luminol, fluorescein, eosin or haemin increases with temperature. In mixed indicator systems, the activation barrier may be overcome by energy transfer during the formation of intermediate complexes, and thus reactions can proceed more rapidly at lower temperatures.

CONCLUSIONS

The chemiluminescent light emitted on oxidation of a luminol-haemin system is undoubtedly from a triplet-singlet transition in the luminol molecule. The intermediate reactions responsible for the excitation of the luminol can, however, be varied by the experimental conditions. The main intermediate is a luminol-oxygen-haemin complex. In mild alkaline conditions most of this complex appears to dissociate leaving the oxygen with the haemin, but under stronger alkaline conditions the oxygen is retained by the luminol with the simultaneous evolution of nitrogen.

There are also competing reactions responsible for the formation of the intermediate association complex. The actual course of the chemical reactions responsible for the activation of luminol therefore varies with the concentrations of luminol, haemin, hydrogen peroxide and alkali present.

In alkaline conditions, the chemical reactions destroy either the luminol or the haemin and hence a mixture of these two cannot be used for the titration of bases by acids. However, since fluorescein is not affected by the alkaline conditions, a mixture of fluorescein-luminol has been found to be a suitable indicator for this type of reaction. The use of a luminol-glycerol mixture as a chemiluminescent indicator was only partially successful, since sufficient glycerol can be oxidised to give an error in the volume of acid required in the titration at the elevated temperature necessary for chemiluminescence.

Acknowledgements—Two of us (L. E. and W. F. P.) acknowledge with thanks the Research Fellowships made available by The Queen's University of Belfast which permitted us to participate in this project.

Zusammenfassung—Untersuchung der Luminiszenz von Hämin-Luminol Mischungen haben gezeigt, dass Hämin eine chemiluminiszente Substanz ist. Ein Mechanismus für die Hämin-Luminol Reaktion wird vorgeschlagen. Der Reaktionsverlauf scheint von der relativen Konzentration der beiden Komponenten und von der Alkalität der Lösung abzuhängen.

Résumé—Une étude de la luminescence de mélanges hemine-luminol a montré que l'hemine est une substance chimioluminescente; les auteurs proposent un mécanisme pour la réaction hemine-luminol. La marche de la réaction dépend des concentrations relatives des composants et de l'alcalinité de la solution.

REFERENCES

[1] C. N. Zellner and G. Dougherty, *J. Amer. Chem. Soc.*, 1937, **59,** 2580.
[2] K. Weber, *Ber.*, 1942, **75B,** 565.
[3] K. Weber, A. Rezek and V. Vouk, *ibid.*, 1942, **75B,** 1141.
[4] K. Weber and M. Krajcinovic, *ibid.*, 1942, **75B,** 2051.
[5] K. Weber, W. Lahm and E. Hieber, *ibid.*, 1943, **76B,** 366.
[6] K. Weber, *Arhiv. Kem.*, 1951, **23,** 173; *Chem. Abs.*, 1953, **47,** 11993.
[7] K. Weber and K. F. Schultz, *ibid.*, 1954, **26,** 173; *Chem. Abs.*, 1955, **49,** 12970.
[8] K. Weber, Z. Prochazka and J. Spoljaric, *Croat. Chem. Acta*, 1956, **28,** 25; *Chem. Abs.*, 1956, **50,** 16404.
[9] K. Weber and R. Kostelac, *ibid.*, 1956, **28,** 33.
[10] K. Weber and J. Frketic, *Arhiv. Hig. Rada*, 1953, **4,** 1; *Chem. Abs.*, 1954, **48,** 4622.
[11] L. K. Klimovakaya and V. E. Shmaevskii, *Dopovidi L'viv. Dorzhav. Univ. im. I Franka*, 1955, **5,** 78; *Chem. Abs.*, 1958, **52,** 9785.
[12] A. A. Ponomarenko, N. A. Merkarjan and A. I. Komlew, *Doklady Akad. Nauk. S.S.S.R.*, 1952, **86,** 115.
[13] F. Kenny and R. B. Kurtz, *Analyt. Chem.*, 1951, **23,** 339.
[14] L. Erdey and I. Buzás, *Acta Chim. Acad. Sci. Hung.*, 1955, **6,** 93, 115, 123.
[15] L. Erdey, *Ind. Chemist*, 1957, 523 and 575.
[16] B. Tamamuski, *Naturwiss.*, 1940, **46,** 722; I. Plotnikow, *Umschau*, 1938, **42,** 981.
[17] L. Erdey, W. F. Pickering and C. L. Wilson, *Talanta*, 1962, **9,** 371.
[18] L. Erdey, *Acta Chim. Acad. Sci. Hung.*, 1953, **3,** 95.
[19] A. White, P. Handler, E. L. Smith and D. Stetten, *Principles of Biochemistry*. McGraw-Hill Book Co., London, 2nd Ed., 1959, p. 202.
[20] A. Goudot, *Compt. rend.*, 1955, **241,** 1944.
[21] R. Brdicka and K. Wiesner, *Coll. Czech. Chem. Comm.*, 1947, **12,** 39.
[22] N. I. Kobozev, *Acta Physicochim., U.R.S.S.* 1946, **21,** 469; *Chem. Abs.*, 1947, **41,** 2309.
[23] C. Reid, *Quart. Rev.*, 1958, **15,** 205.
[24] C. A. Parker and C. J. Hatchard, *Trans. Faraday Soc.*, 1961, **57,** 1894.
[25] L. Erdey and I. Buzás, *Analyt. Chim. Acta*, 1960, **22,** 524.

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APPLICATIONS OF INFRARED SPECTROSCOPY—IX*

THE DIFFERENTIATION OF ESTERS AND ACETALS FROM ETHERS IN THE ZEISEL ALKOXYL REACTION

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(*Received* 30 *January* 1962; *Accepted* 5 *February* 1962)

Summary—After determination of the total alkoxyl content (ester + ether groups) by reflux with hydriodic acid, the contribution from methyl and ethyl ester groups is found by refluxing a second sample of the compound in constant-boiling hydrochloric acid for 3 hr. Acetals cannot be distinguished from esters; the yields of alkyl chloride from propyl and butyl esters are diagnostic, although not quantitative. Certain classes of compounds, which have unusually labile ether linkages, restrict the general applicability of the method; examples of such compounds are given.

THE Zeisel alkoxyl determination gives the total alkoxyl content of a compound, and does not differentiate[1] between esters, acetals, alcohols and ethers; such information would be useful in structural studies on complex molecules.

Analytical methods for esters[2] and acetals[3] have been reviewed: colorimetric[4] and oximation[5] methods for determining acetals, ketals and vinyl ethers continue to be described. Differences in reaction-rate can sometimes be used to analyse mixtures of organic compounds containing the same functional group.[6,7] The Zeisel reaction-time for quantitative yields of alkyl iodide from methoxy and ethoxy compounds is so rapid, however (approx. 15 min for methyl iodide) that kinetic differentiation between esters and ethers is not feasible (*cf.* ref. 8).

Methods for the determination of methanol, methyl esters and methyl ethers were considered in an early review,[9] and the determination of glycosidic methoxyl was investigated by Hoffpanir and Reeves.[10] The use of hydrobromic acid as a demethylating agent is well known;[11,12] when it was found[13] that constant-boiling hydrobromic acid produced alkyl bromides quantitatively from esters and ethers almost as quickly as hydriodic acid formed the corresponding iodides (*cf.* refs. 12 and 14), the rates of reaction in constant-boiling hydrochloric acid were investigated. Quantitative yields of the corresponding alkyl chloride were obtained from methyl or ethyl esters and acetals in 3 hours; in that time, only trace amounts of alkyl chloride were produced from true ethers (*e.g.*, 0·05 moles from vanillin, 0·12 moles from 2,3-dimethoxybenzaldehyde, 0·02 moles from phenacetin) (*cf.* ref. 15). This modification to the Zeisel reaction therefore gives the possibility of differentiating between esters and ethers.

EXPERIMENTAL

The reagents, reaction conditions and apparatus used for determination of total alkoxyl, using constant-boiling hydriodic acid, were as described elsewhere.[16] The ester content is found by refluxing a sample (sufficient to yield 1–4 mg of alkyl chloride) for 3 hr with constant-boiling hydrochloric acid (6 ml) to which approx. 0·25 g of phenol has been added.

* Part VIII: D. M. W. Anderson, M. A. Herbich and S. S. H. Zaidi, *Talanta*, 1962, **9**, 620.

† Present address: Dept. of Chemistry, The University, Reading, England.

The alkyl chloride evolved is determined by the infrared method, using the manometric method of calibration:[17] laboratories not equipped with an infrared spectrometer can use a modified Fujiwara method.[18]

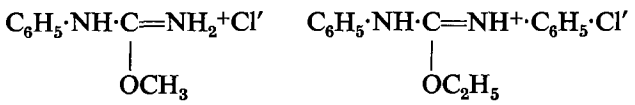
No difficulty was experienced with volatile alcohols, acetals and esters when the reaction conditions proposed by Anderson and Duncan[16] were used (*cf.* refs. 19 and 20).

RESULTS

The method has been applied to a wide range of methoxy and ethoxy compounds having (*a*) ether groups only, (*b*) ester groups only, and (*c*) ether and ester groups in various combinations. Some typical results are shown in Tables I and II, together with the structural deductions possible had only the molecular weight of the compound been known.

Whilst the method is clearly applicable to many compounds, it is not of general applicability. Several classes of compound contain abnormally reactive ether groups, which are labile in constant-boiling hydrochloric acid. The following examples of these have been encountered in this work, and others doubtless exist (*cf.* ref. 12):

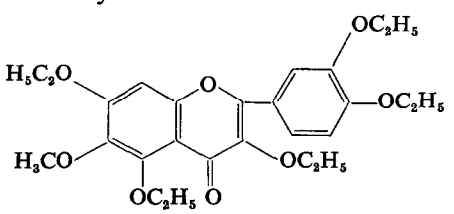
(1) *Substituted urea salts,* such as X and XI.



X XI

(2) *Certain methoxy-pyrimidines*[21] *and -pyridines.*[22]

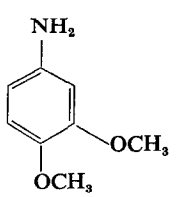
(3) *Flavone derivatives*[23] containing alkoxyl substituents at position 5. Thus 3,5,7, 3′,4′-pentaethoxy-6-methoxyflavone (XII) gives 1 mole of ethyl chloride (from position 5) when treated with hydrochloric acid, and 1 mole of methyl iodide + 5 moles of ethyl iodide on reflux with hydriodic acid.



XII

Reaction with constant-boiling hydrochloric acid is therefore a diagnostic test for alkoxyl substituents at position 5 in flavones if it is known (infrared spectroscopy) that ester groups are not also present in the molecule.

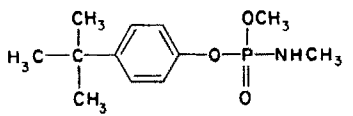
(4) *Certain dimethoxy compounds,*[24] such as the *N*-benzene-sulphonyl derivative of XIII.



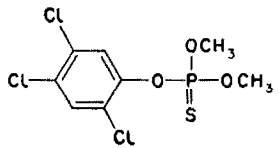
XIII

TABLE I.

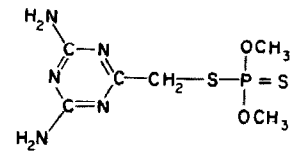
Compound	Reflux with hydriodic acid: total methoxyl, % Theory	Found	total ethoxyl, % Theory	Found	Reflux with hydrochloric acid: ester methoxyl, % Theory	Found	ester ethoxyl, % Theory	Found	Deductions
Vanillin	20·4	20·4	—	—	0	0·9	—	—	ether groups only.
Phenacetin	—	—	25·2	25·1	—	—	0	0·5	
Yohimbine HCl	7·94	7·92	—	—	7·94	7·67	—	—	ester groups only.
Ethyl-*p*-nitrobenzoate	—	—	23·1	22·9	—	—	23·1	22·7	
"Ruelene" (I)	10·7	10·5	—	—	10·7	10·5	—	—	
"Ronnel" (II)	19·3	19·3	—	—	19·3	19·0	—	—	
"Menazon" (III)	22·1	21·4	—	—	22·1	21·2	—	—	
"Mecarbam" (IV)	—	—	41·0	40·6	—	—	41·0	40·1	
Methyl anisate	37·4	37·4	—	—	18·7	19·2	—	—	methyl ether and ester groups, ratio 1:1
Methyl-3:4-dimethoxybenzoate	47·4	47·3	—	—	15·8	16·1	—	—	methyl ether and ester groups, ratio 2:1
Reserpine	30·6	30·4	—	—	5·10	5·36	—	—	methyl ether and ester groups, ratio 5:1
Methyl mangifate trimethyl ether (V)	29·7	29·3	—	—	7·43	7·71	—	—	methyl ether and ester groups, ratio 3:1
Ethyl-α-ethoxypropionate	—	—	61·6	61·2	—	—	30·8	31·7	ethyl ether and ester groups, ratio 1:1



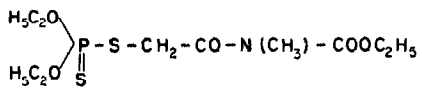
I



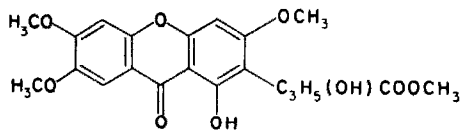
II



III



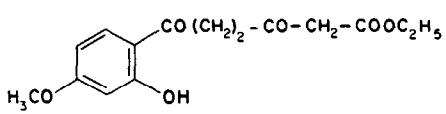
IV



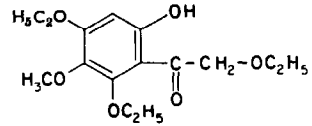
V

TABLE II

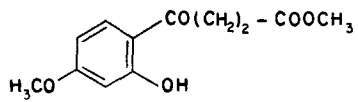
Compound	Reflux with hydriodic acid				Reflux with hydrochloric acid				Deductions
	total methoxyl, %		total ethoxyl, %		ester methoxyl, %		ester ethoxyl, %		
	Theory	Found	Theory	Found	Theory	Found	Theory	Found	
Methyl-3-ethoxy-4-methoxybenzoate	29·5	29·3	21·4	21·1	14·7	15·0	—	—	methyl ester, methyl and ethyl ether, ratio 1:1:1.
Ethyl-3:4-dimethoxy-benzoate	29·5	29·3	21·4	21·6	—	—	21·4	20·8	all ethoxyl present as ester, all methoxyl as ether. Ratio of methoxy/ethoxy = 2/1.
(VI)	10·0	10·3	14·5	14·1	—	—	14·5	13·9	all ethoxyl present as ester, all methoxyl as ether. Ratio of methoxy/ethoxy = 1/1.
(VII)	26·0	26·0	—	—	13·3	13·0	—	—	methoxy only; ratio of ester/ether = 1/1.
2-hydroxy-5-methoxy-w4:6-triethoxy-acetophenone (VIII)	10·4	10·6	45·3	44·7	—	—	—	—	methoxy and ethoxy, present as ethers only. Ratio = 1/3.
Ethyl angolensin (IX)	10·3	10·0	15·0	14·8	—	—	—	—	methoxy and ethoxy, present as ethers only. Ratio = 1/1.



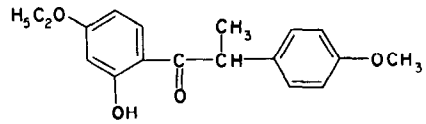
(VI)



(VIII)



(VII)



(IX)

(5) *Compounds containing tertiary butyl*[25] *groups.* Two effects must be distinguished: (*a*) non-alkoxy tert-butylated compounds yield alkyl halide, so giving an anomalous reaction; (*b*) in certain alkoxy tert-butylated compounds, such as tert-butylated-*p*-hydroxyanisole, both the tert-butyl and alkoxyl groups are labile so that the compound does not react like a true ether. In addition, high alkoxyl results are given if a method which does not differentiate between methyl and tert-butyl halides is used (*cf.* refs. 8 and 26).

(6) *Methyl glycosides and* O-*methyl carbohydrate derivatives.* A method for differentiating between methyl ester groups at C_6 and methyl linkages at C_2, C_3 and C_4 would be of great value in investigations of plant gums[27] and pectins; investigations of mild de-alkylating reagents[22] are in progress.

Propyl and butyl esters give non-quantitative yields of the corresponding alkyl chloride (approx. 70% for propyl, 30% for butyl chloride) even when zinc chloride is added to the reaction mixture. It is well-known, however, that propyl and butyl ethers react much more slowly in acid solutions than methyl or ethyl ethers. Small yields of propyl and butyl chlorides on reflux with constant-boiling hydrochloric acid therefore indicate the presence of the corresponding ester groups. (The exceptional case of tert-butyl groups has already been mentioned.)

Acknowledgements—We are grateful for gifts of the compounds indicated, to:—Dow Chemical Co. (compounds I and II); Plant Protection Ltd. (III); Murphy Chem. Co., St. Albans (IV); Miss D. A. Thomson, University of Aberdeen (VI and VII); Dr. R. A. Laidlaw and Dr. J. Morgan, Forest Products Research Laboratory, D.S.I.R., Princes Risborough (V, VII, IX, XII). We thank the Carnegie Trust for the award of a scholarship (to J. L. D.).

Zusammenfassung—Nach Bestimmung des geamten Alkoxylgehaltes (Ester- und Ätherguppen) mittels Rückflussdestillation mit Iodwasserstoffsäure, wird der Anteil der Methyl- und Äthylgruppen durch Rückflussdestillation (3 Stunden) mit konstant siedender Salzsäure bestimmt. Acetale können von Äthern nicht differenziert werden. Die Ausbeuten der Alkylchloride von Propyl- und Butylestern sind nicht quantitativ, haben aber diagnostischen Wert. Gewisse Klassen von Komponenten mit besonders labilen Ätherbindungen begrenzen die allgemeine Anwendbarkeit der Methode. Beispiele für solche sind mitgeteilt.

Résumé—Après dosage de la teneur totale en alcoyle (groupes ester + éther-oxyde) par reflux avec l'acide iodhydrique, la contribution des groupes esters méthylique et éthylique est déterminée en chauffant au reflux un deuxième échantillon du composé dans de l'acide chlorhydrique bouillant constamment pendant trois heures. Les acétals ne peuvent pas être distingués des éther-oxydes; les rendements en chlorure d'alcoyle à partir des esters propylique et butyrique sont déterminés, bien que non quantitatifs. Certaines catégories de composés, qui possèdent des liaisons étheroxyde inhabituellement labiles, restreignent l'application générale de la méthode; des exemples de tels composés sont donnés.

REFERENCES

[1] S. Zeisel and R. Fanto, *Z. Landw. versuch. Osterreich.*, 1902, **5**, 729.
[2] R. T. Hall and W. E. Shaefer, *Organic Analysis*, Vol. II. Interscience Pub. Inc., New York, 1954, p. 19.
[3] J. Mitchell, *Organic Analysis*, Vol. I, 1953, p. 309.
[4] M. C. Bowman, M. Beroza and F. Acree, *Analyt. Chem.*, 1961, **33**, 1053.
[5] B. Budesinsky and J. Körbl, *Mikrochim. Acta*, 1960, 697.
[6] T. S. Lee, *Organic Analysis*, Vol. II, 1954, p. 237.

[7] S. Siggia and J. G. Hanna, *Analyt. Chem.*, 1961, **33**, 896.
[8] D. M. W. Anderson and J. L. Duncan, *Chem. and Ind.*, 1959, 457.
[9] T. von Fellenberg, *Biochem. Z.*, 1918, **85**, 45.
[10] C. L. Hoffpanir and R. E. Reeves, *Analyt. Chem.*, 1949, **21**, 815.
[11] L. Hough, J. K. N. Jones and W. H. Wadman, *J. Chem. Soc.*, 1950, 1702.
[12] R. L. Burwell, *Chem. Revs.*, 1954, **54**, 677.
[13] D. M. W. Anderson and J. L. Duncan, *Talanta*, 1961, **8**, 1.
[14] L. C. Raiford and J. C. Colbert, *J. Amer. Chem. Soc.*, 1926, **48**, 2652.
[15] R. Stoermer, *Ber.*, 1908, **41**, 321.
[16] D. M. W. Anderson and J. L. Duncan, *Talanta*, 1960, **7**, 70.
[17] D. M. W. Anderson, *Analyst*, 1959, **84**, 50.
[18] M. Redford-Ellis and J. E. Kench, *Analyt. Chem.*, 1960, **32**, 1803.
[19] D. O. Hoffman and M. L. Wolfrom, *ibid.*, 1947, **19**, 225.
[20] A. Steyermark, *ibid.*, 1948, **20**, 368.
[21] T. L. V. Ulbricht, *Tetrahedron*, 1959, **6**, 225.
[22] Idem, *J. Chem. Soc.*, 1961, 3345.
[23] F. Sondheimer and A. Meisels, *Tetrahedron*, 1960, **9**, 139.
[24] J. A. F. Gardner, R. Y. Moir and C. B. Purves, *Canad. J. Chem.*, 1948, **26**, 681.
[25] J. F. Norris and G. W. Rigby, *J. Amer. Chem. Soc.*, 1932, **54**, 2088.
[26] A. D. Campbell and V. J. Chettleburgh, *Analyst*, 1959, **84**, 190.
[27] K. Selby, *J. Chem. Soc.*, 1953, 2504.

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ANALYTICAL APPLICATIONS OF INFRARED SPECTROSCOPY

IDENTIFICATION OF POLYATOMIC INORGANIC ANIONS

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(*Received* 2 *March* 1962. *Accepted* 30 *March* 1962)

Summary—Using infrared absorption spectroscopy a method has been developed which permits the identification of the following 14 anions: pertechnetate, perrhenate, thiocyanate, persulphate, perchlorate, chlorate, permanganate, periodate, ferricyanide, ferrocyanide, thiosulphate, chromate (or dichromate), molybdate and tungstate. The method is fast, sensitive and reliable compared to the corresponding laborious and time-consuming classical methods.

ALTHOUGH a large number of investigations of inorganic compounds by infrared absorption spectroscopy has been carried out, few applications of this technique to systematic qualitative analysis have been attempted. Hunt *et al.*,[1] studied the infrared absorption spectra of 64 natural minerals and compounds, while Miller and Wilkins[2] carried out their investigations on a number of inorganic salts, building up an excellent catalogue for 159 compounds.

In the present work infrared spectroscopy was used in the systematic identification of the following anions: pertechnetate, perrhenate, thiocyanate, persulphate, perchlorate, chlorate, permanganate, periodate, ferricyanide, ferrocyanide, thiosulphate, chromate (or dichromate), molybdate and tungstate.

All of the foregoing anions form compounds of the type $(Phenyl)_4AsX$, where X is the anion, and the method used is based on the precipitation of the anions with tetraphenylarsonium chloride (TPAC), followed by the mixing of the precipitate with potassium bromide. From the mixture a disc was prepared. This disc, when placed in the infrared spectrophotometer, produced spectra which permitted the identification of the anions present.

EXPERIMENTAL

Apparatus and reagents

The infrared spectra were recorded on a Perkin-Elmer ('Infracord') Spectrophotometer, Model 137.

The potassium bromide discs were prepared with a Perkin-Elmer die using an 'Apex' hydraulic press with a 10-ton capacity on a ram of $2\frac{1}{8}$-inch diameter. Before use, the potassium bromide, which was Analytical Reagent grade, was dried at 150° for 24 hr. The tetraphenylarsonium chloride was supplied by L. Light and Co., Ltd. A 10% aqueous solution was used.

All other chemicals used in the work were AnalaR.

Procedure

1. Dissolve an appropriate amount (about 5–50 mg) of the anion mixture in approximately 3 ml of water or suitable solvent in a 20-ml centrifuge tube. Add sufficient solid sodium chloride to make the solution about 1*M*. Neutralise with ammonia solution and add 0·5 ml in excess. Heat the solution, centrifuge and discard any precipitate formed.

2. Add to the clear solution an excess of 10% tetraphenylarsonium chloride reagent. Mix the contents for a few min and centrifuge. To the supernatant liquid add 1 more drop of TPAC reagent to ensure that precipitation is complete. Decant into a second centrifuge tube, wash the precipitate

with 1 ml of 1*M* sodium chloride solution and centrifuge once more. Decant the washings into a second centrifuge tube. Dry the precipitate by placing the tube in a water bath maintained at a temperature of 50–60°. Connect the tube to a vacuum pump. This prevents decomposition of some complexes. The precipitate will contain thiocyanate, persulphate, perchlorate, chlorate, perrhenate, pertechnetate, permanganate and periodate, if these anions were present in the original mixture.

3. Scrape out the precipitate with a small spatula and break up any lumps which may have formed. Weigh out 1–3 mg of the precipitate and approximately 300 mg of potassium bromide. Transfer to an agate mortar. Grind the mixture to a fine state of division and place in the die.

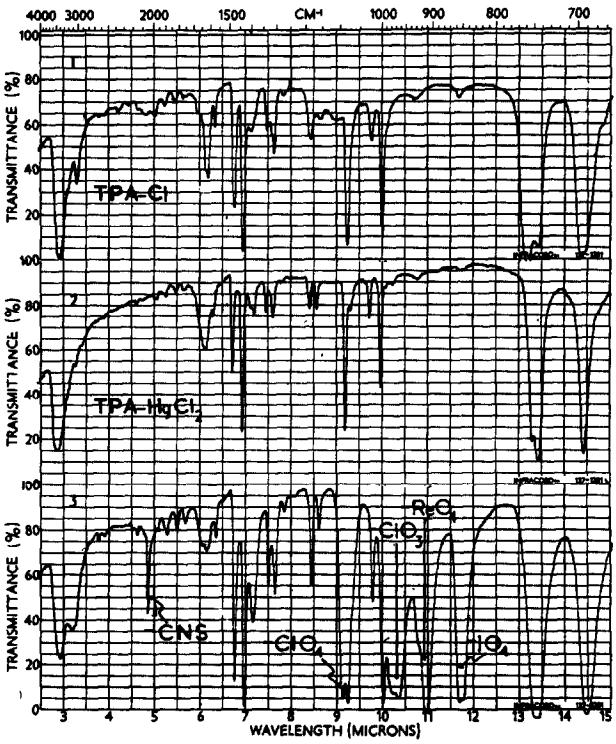


FIG. 1. 1—Tetraphenylarsonium chloride (TPAC). 2—Tetraphenylarsonium chloromercuriate. 3—Tetraphenylarsonium complexes of thiocyanate, perchlorate, chlorate, perrhenate and periodate.

Evacuate the assembled die for 2 min and apply a total pressure of 10 tons for a period of 5 min. Dismantle the die and fix the disc with a special holder in the beam of the 'Infracord' spectrophotometer using a disc of potassium bromide in the reference beam. Record the spectrum over the range 3–15 μ. The characteristic bands of each anion are shown in Figs. 1, 2 and 3.

4. Divide the supernatant liquid from the TPAC precipitation into 2 parts. To one part add a small strip of litmus paper and neutralise the solution with 1:1 hydrochloric acid, adding a drop in excess. The formation of a precipitate in this operation indicates the presence of ferrocyanide, ferricyanide, thiosulphate, chromate (or dichromate), molybdate and tungstate.

Centrifuge and add 1 drop of TPAC reagent to ensure complete precipitation. Treat the precipitate as outlined above, and record the spectrum over the range 3–15 μ. The spectra are shown in Figs. 1, 2 and 3.

5. If chromate, molybdate and tungstate are present, their interference may be eliminated by adding to the second portion of the solution approximately 0·1 g of sodium citrate or citric acid and treating the solution as under (4) above.

RESULTS AND DISCUSSION

Tetraphenylarsonium chloride was introduced as an analytical reagent by Willard and Smith.[3] It forms precipitates under different conditions with a large number of

ions, *e.g.* iodide, bromide, fluoride, bismuth^{III}, platinum^{IV}, gold^{III}, palladium^{IV}, tin^{IV}, zinc^{II}, cadmium^{II}, thallium^{III}, mercury^{II}, the metallic complexes of thiocyanate and other groups, as well as with the polyatomic anions examined in this study. The solubilities of these precipitates range from fairly soluble, *e.g.* chlorate, thiosulphate, ferrocyanide, ferricyanide, and tungstate, to sparingly soluble, *e.g.* perrhenate, pertechnetate, perchlorate, *etc.* If the former groups of anions are present in microgram quantities, then complete precipitation will be assisted by the presence of the latter group which behaves as a carrier. The method is reasonably sensitive, 10 μg or even less of perrhenate, pertechnetate, thiocyanate and periodate in a 300-μg potassium bromide disc can be detected, and it is possible to detect amounts of less than 100 μg of the fairly soluble precipitate such as chlorate and thiosulphate.

The characteristic infrared spectra of polyatomic inorganic compounds under normal conditions are caused by rotation in addition to the lattice vibrations and their absorption bands are, in general, broad and in some cases ill-defined. This makes their identification difficult, particularly in mixtures. Exceptions are the simple or complex cyanides which exhibit sharp bands from C–N stretching frequencies.

The characteristic bands of the polyatomic anions examined in this study are attributable to either metal-oxygen frequencies, as in perrhenate, or to non-metal-oxygen frequencies, as in persulphate, *etc.* It was found that most of the metal-oxygen frequencies fall within the range of 9–11 μ.[4] The advantages of using TPAC as a precipitant for the isolation of the anions prior to infrared absorption studies can be summarised as follows:

(1) The reagent forms ion-association complexes with a large number of ions. These complexes are mostly insoluble and can be separated from other interfering ions.

(2) Although the reagent has a comparatively high molecular weight and is composed of several groups, it exhibits a relatively simple infrared spectrum and has few strong absorption bands. These cause no interference with any of the anions investigated in the present study.

(3) The bonds between the anions and the TPA ion are covalent in character, which leads to sharper bands with less overlapping than obtained with the pure inorganic compounds. Perrhenate, pertechnetate, and permanganate (when complexed with TPAC) exhibit strong bands at 10·94, 11·09, and 11·02 μ.

Perrhenate, pertechnetate and permanganate

It is quite easy to identify perrhenate, pertechnetate and permanganate (Fig. 2) if present singly, but identification can be difficult if these anions are present together in a mixture.

From the infrared spectra of these anions it is evident that they are isomorphous and the presence of one strong band may mean that they are monomers. The strong bands are assignable to metal-oxygen stretching frequencies (M = 0). These complexes are soluble in chloroform.

Molybdate and tungstate

These two anions show several absorption bands at longer wavelengths (Fig. 3). The intensities of the bands are variable. This may be explained on the basis that these ions exist as polymers, the presence of several bands arising from M—O—M—O continuous structures.[4] The variability of the bands can also be attributed to the

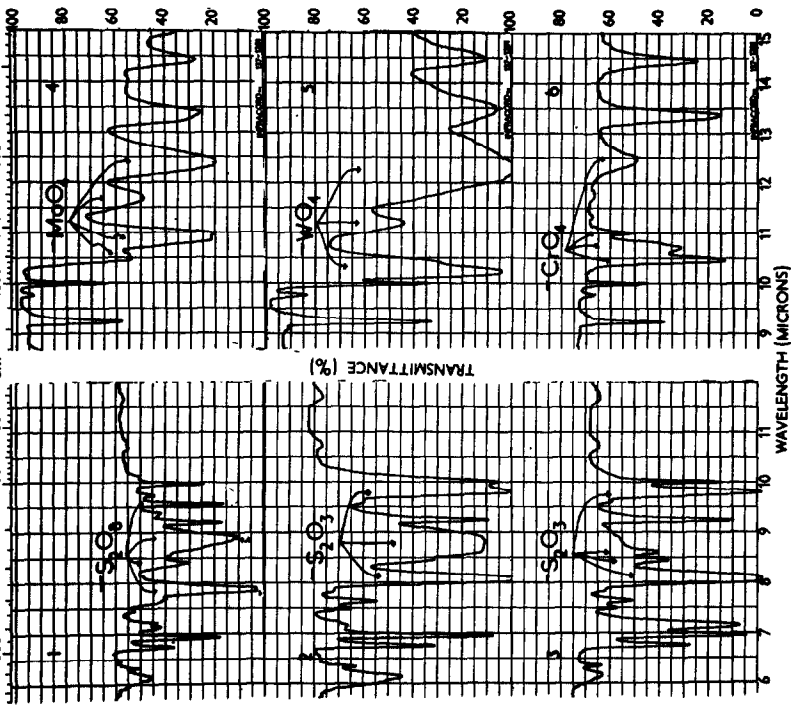


FIG. 3. 1—Tetraphenylarsonium persulphate. 2—Tetraphenylarsonium thiosulphate (from neutral solution). 3—Tetraphenylarsonium thiosulphate (from slightly acidic solution). 4—Tetraphenylarsonium molybdate. 5—Tetraphenylarsonium tungstate. 6—Tetraphenylarsonium chromate (or dichromate).

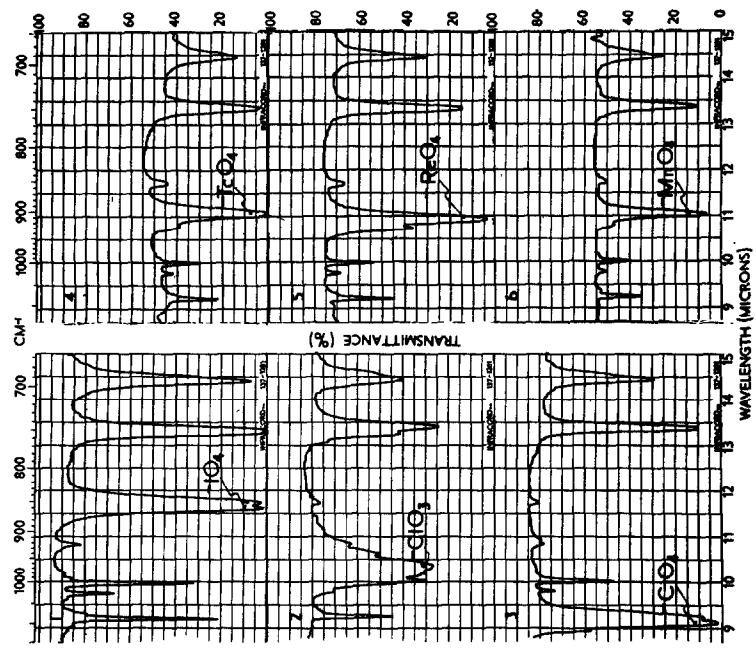


FIG. 2. 1—Tetraphenylarsonium periodate. 2—Tetraphenylarsonium chlorate. 3—Tetraphenylarsonium perchlorate. 4—Tetraphenylarsonium pertechnetate. 5—Tetraphenylarsonium perrhenate. 6—Tetraphenylarsonium permanganate.

variability of composition of the complexes under different conditions. Identification can be difficult, especially when present with chromate ions. These complexes are insoluble in chloroform. Addition of citrate ion prevents the precipitation of molybdate and tungstate complexes.

Chromate (or dichromate)

The procedure outlined permits the identification of chromate (or dichromate) ion which is characterised by a strong band at 10·48 μ and other variable bands (Fig. 3). The disappearance of the absorption bands on the addition of citrate ions can be used as a confirmation of the presence of molybdate and tungstate ions. On the other hand the treatment of chromate ion with iron^{II} sulphate and the consequent elimination of the strong band at 10·48 μ can be regarded as a confirmation of the presence of this ion.

Ferrocyanide and ferricyanide

Ferrocyanide and ferricyanide ions form precipitates from a slightly acidic medium, and the infrared spectra of their precipitates show strong and sharp bands at 4·65 and 4·74 μ, respectively. Although these two bands are close to each other there is no overlapping, which permits their individual identification when present in approximately equal amounts.

Perchlorate and chlorate

The perchlorate ion forms a stable complex and exhibits a strong and sharp band at 9·12 μ. Although this band and that exhibited by the reagent at 9·24 μ partially overlap, the identification of microgram quantities of perchlorate ion is still easy (Fig. 1). The chlorate ion which forms a fairly soluble complex with TPAC exhibits a strong and broader band at 10·35 μ. The broadness may be explained by the assumption that the bonding between the chlorate ion and TPA ion is less covalent in character than in the other cases discussed. To identify a microgram amount of chlorate ion by the infrared technique, a carrier such as the perchlorate ion must also be present.

Persulphate and thiosulphate

The persulphate ion forms an apparently stable complex with TPAC which is insoluble in water. This ion shows several strong bands (Fig. 3).

Thiosulphate ion forms a fairly soluble complex with TPAC under neutral and slightly acidic conditions. The complex formed in neutral solution exhibits three absorption bands at 8·08, 8·78, and 9·8 μ. The band at 8·78 μ is variable and broad. When the complex is formed in a slightly acidic medium the broad band at 8·78 μ splits into two weaker bands.

Thiocyanate

Thiocyanate ion forms an insoluble precipitate with TPAC in alkaline and acidic media. It shows a strong and sharp band at 4·85 μ which permits the identification of a few μg in a 300-mg potassium bromide disc (Fig. 1).

Periodate

With TPAC in acidic or alkaline media this ion forms a precipitate which shows a strong absorption band at 11·68 μ (Fig. 2).

It is worthy of note that the TPA complexes of most of the anions examined in this work show two very weak absorption bands at approximatley 10·8 μ and 11·7 μ. In no case, however, did these bands ever interfere with the detection of perrhenate, pertechnetate, permanganate or periodate. Comparison of the spectra of the anions concerned and that of the reagent removes any misinterpretation which might arise.

Other anions

TPAC forms precipitates with fluoride, bromide and iodide, which interfere in the precipitation of the anions studied in the present work. Fortunately, however, the halide complexes of (TPAC) show spectra which are similar to (TPAC) in the region from 3–15 μ.

The halo-complexes of some metallic ions, such as $(HgCl_4)^{2-}$, with the TPA ion form precipitates which do not exhibit a significant band in the working region (Fig. 1). If, therefore, these ions are present, no interference in the identification of the other anions arises.

Zusammenfassung—Eine infrarotspektrophotometrische Methode wurde entwickelt um die folgenden 14 Anionen rasch, empfindlich und zuverlässig zu bestimmen und das besser und schneller als nach klassischen Methoden: Pertechnat, Perrhenat, Thiocyanat, Persulfat, Perchlorat, Chlorat, Permanganat, Perjodat, Ferri- und Ferrocyanid, Thiosulfat, Chromat (und Dichromat), Molybdate und Wolframat.

Résumé—Les auteurs ont mis au point une méthode de spectroscopie d'absorption infra-rouge permettant l'identification des 14 anions suivants: pertechnétate, perrhénate, thiocyanate, persulfate, perchlorate, chlorate, permanganate, périodate, ferricyanure, ferrocyanure, thiosulfate, chromate (ou bichromate), molybdate et tungstate. La méthode est rapide, sensible et fidèle par comparaison avec les méthodes classiques correspondantes longues et laborieuses.

REFERENCES

[1] J. M. Hunt, M. P. Wisherd and L. C. Bonham, *Analyt. Chem.*, 1950, **22**, 1478.
[2] F. A. Miller and C. H. Wilkins, *ibid.*, 1952, **24**, 1253.
[3] H. H. Willard and G. M. Smith, *Ind. Eng. Chem., Analyt.*, 1939, **11**, 186, 269, 305.
[4] C. G. Barraclough, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, 1959, 3552.

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THE SPECTROPHOTOMETRIC DETERMINATION OF SULPHUR IN IRON ALLOYS

METHYLENE BLUE METHOD

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Summary—Sulphur is determined in iron alloys by evolution as hydrogen sulphide, followed by reaction with *N,N*-dimethyl-*p*-phenylenediamine and iron^{III} to form methylene blue, which is measured spectrophotometrically. Replicate results are reported for acid soluble metal samples containing 0·3-230 ppm of sulphur. An evaluation of the accuracy of the methylene blue procedure was made using radiotracer techniques.

INTRODUCTION

TRACES of sulphur have a marked effect on the physical properties of steel and other iron-base alloys; consequently, the accurate determination of small amounts of sulphur in these materials is of considerable importance. Traditional techniques for this analysis may be summarised as follows: (1) precipitation of sulphur as barium sulphate following solution of the sample in an oxidising medium; (2) combustion of the sample in oxygen and absorption of the sulphur oxides in an aqueous iodine solution, followed by measurement of the sulphur by a redox titration or by a colorimetric technique; or (3) evolution of hydrogen sulphide from a hydrochloric acid solution of the sample followed by absorption and determination of the sulphide by a redox titration. These techniques were found to be unsatisfactory for the determination of less than 10 ppm of sulphur when sample size was limited to 5 g or less. The use of more than 5 g of sample is impractical by the combustion technique; and dissolution of a sample of this size is slow and introduces large quantities of other elements.

The method herein proposed involves the reaction between sulphide, *N,N*-dimethyl-*p*-phenylenediamine and iron^{III}, which produces the intense blue colour of methylene blue. While this system has been known for some time[1,2,6] it has not previously been applied to the determination of sulphur in ferruginous materials. Fogo and Popowsky[3] first used modern spectrophotometric instrumentation in the study of the methylene blue techniques. The experimental conditions suggested by their work were applied in our laboratory to the determination of 2–250 μg of sulphur in 0·1–4 g of iron-base alloys. Recently, Gustafsson[4] investigated thoroughly a number of variables in the methylene blue system, including temperature, acidity, various anions, traces of heavy metals, ageing time, reagent concentrations and air-oxidation.

APPLICABILITY

This procedure may be used to determine sulphide sulphur in any sample in which the sulphide is soluble in dilute hydrochloric acid. Materials studied thus far include a variety of iron alloys and manganese. If the sulphur is present as the sulphate, the

reduction solution technique detailed by Gustafsson[5] is used before determining the sulphur.

EXPERIMENTAL

Reagents

All reagents are prepared with de-ionised water rather than with distilled water.

Ferric Chloride: 6·2 g of $FeCl_3 \cdot 6H_2O$ in 400 ml of 1·2*N* hydrochloric acid.

Hydrochloric Acid: 6*N*.

Nitrogen, Liquid: Used as the source for all gaseous nitrogen because of excessive oxygen in tank nitrogen.

N,N-*Dimethyl*-p-*phenylenediamine Monohydrochloride:* 0·5 g in 500 ml of 6*N* hydrochloric acid.

Potassium Iodate: Standard solution, 0·03*N*, containing 20 g of potassium iodide in 1 litre of water.

Sodium Hydroxide: 12 g in 100 ml of water.

Starch Solution: 1 g in 100 ml of water.

Zinc Acetate: 10 g in 1 litre of water.

Apparatus

See Fig. 1. The Westinghouse Electric Corporation will make and provide equipment of this type if required.

Preparation of standard curve

1. Dissolve 3·5–4·0 g of water-washed crystals of $Na_2S \cdot 9H_2O$ in about 500 ml of cooled freshly-boiled water.
2. Bubble gaseous nitrogen through the solution in a stoppered bottle for 15 min.
3. Store this solution under a slight nitrogen pressure.
4. Remove 2 ml of the sulphide solution through a serum stopper and place in a stoppered 250-ml flask containing 50 ml of cooled, freshly-boiled water.
5. Add 1 ml of starch solution and 10 ml of 6*N* HCl through a serum stopper.
6. Titrate without delay with the KIO_3 solution until a permanent blue colour is obtained.
7. Repeat steps 4, 5 and 6 until a constant value for the titre of the sulphide solution is obtained. (This solution is stable for 3 weeks under nitrogen.)
8. Prepare a dilute sulphide solution by transferring 3 ml of the standard solution to 497 ml of cooled, boiled distilled water, which has been flushed with nitrogen for 30 min. (This solution is stable for 3 days under nitrogen.)
9. Add 50 ml of the $Zn(C_2H_3O_2)_2$ solution and 2 ml of the NaOH solution to the absorption flask.
10. Add 0, 1, 2, 3, 4, 5, or 6 ml of the dilute sulphide solution to the absorption flask.
11. Add, through the serum stopper, 10 ml of *N*,*N*-dimethyl-*p*-phenylenediamine, and swirl until a clear solution is obtained. Temperature should be 24 ± 3°.
12. Add 2 ml of $FeCl_3$ solution through the serum stopper, shake vigorously for 5 sec and age for 15-20 min out of direct sunlight.
13. Transfer the solution to a 100-ml volumetric flask and dilute to volume.
14. Measure the optical density in 2-cm cells at 670 mμ versus water with a Beckman DU Spectrophotometer.
15. Plot results to obtain a standard curve.
16. For lower concentrations of sulphur prepare a similar curve using 10-cm cells.

Analysis of samples

1. Clean samples by swirling with benzene, then with acetone, then air dry.
2. Weigh a sample containing 2-35 μg of sulphur and place in a clean digestion flask.
3. Prepare the absorption flask by adding 50 ml of $Zn(C_2H_3O_2)_2$ solution and 2 ml of NaOH solution.
4. Assemble distillation apparatus and sweep system for 30 min at a moderate rate with nitrogen. Also outgas 50 ml of 6*N* hydrochloric acid with nitrogen for 30 min.
5. Admit water to the condenser, add the outgassed HCl to the reaction flask through the dropping funnel, close stop-cock, and increase the temperature gradually until the boiling point of the solution is reached. (Avoid excessive foaming by control of temperature.)
6. After the sample has dissolved completely, continue sweeping for 60 min. (Occasionally dark material of low density remains undissolved. This is primarily silicon, and may be neglected.)
7. Disconnect absorption flask, close exit tube, add 10 ml of *N*,*N*-dimethyl-*p*-phenylenediamine through the serum stopper and swirl until a clear solution is obtained. Temperature should be 24 ± 3°.
8. Add 2 ml of $FeCl_3$ solution through the serum stopper, shake vigorously for 5 sec, and age for 15-20 min out of direct sunlight.

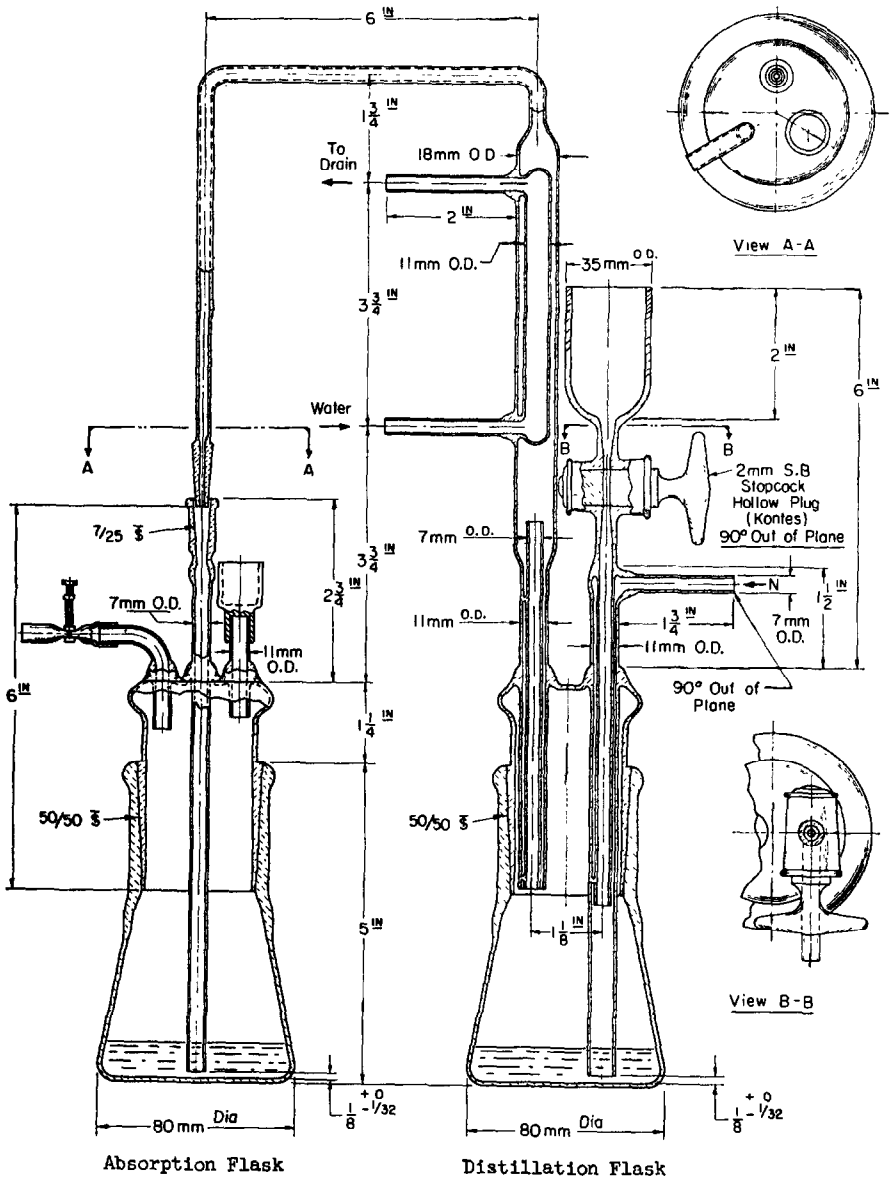


FIG. 1.—Sulphur distillation apparatus.

9. Transfer the solution to a 100-ml volumetric flask and dilute to volume.
10. Measure the optical density with a Beckman DU Spectrophotometer in 2-cm cells at 670 mμ versus water. Use 10-cm cells for low concentrations of sulphur.
11. Subtract optical density of a blank from observed optical density and compare with standard curve to obtain the weight of sulphur in the sample.

RESULTS AND DISCUSSION

Distillation technique

A study was made to determine if sulphur was lost during the solution and distillation phases of the procedure. A second receiver containing zinc acetate and

sodium hydroxide was connected to the first absorption flask and a sample containing 20 μg of sulphur was dissolved and distilled in the usual manner. No sulphur was detected in the second absorption flask. To determine if any sulphide sulphur was retained in the initial reaction vessel an iron-base alloy, doped with radiotracer ^{35}S, was dissolved in an oxidising medium, treated with a known amount of sulphuric acid, and then with barium chloride to precipitate barium sulphate. This precipitate had a specific activity of 10,000 counts per min. A second portion of this alloy was dissolved with hydrochloric acid in the distillation apparatus and the hydrogen sulphide distilled in the normal manner. The residue in the reaction flask was then oxidised and treated with the same amount of sulphuric acid and barium chloride as the first sample. The specific activity of this precipitate was only 5 counts per min with the same counting geometry, thus demonstrating that only a negligible amount of sulphur remained undistilled.

Insoluble residue

Certain iron-silicon alloys did not dissolve completely in constant-boiling hydrochloric acid, but formed dark-coloured flakes of material in addition to the usual silica. This material gradually became translucent upon exposure to air and was identified as silicon metal. To ascertain if sulphur was retained by this material, or by the silica, several samples were treated with a few ml of hydrofluoric acid in addition to the hydrochloric acid usually used to dissolve these materials. The sulphur content of samples dissolved with hydrofluoric and hydrochloric acid combinations was found to be identical with that obtained for samples dissolved with hydrochloric acid alone.

Interferences

Gustafsson[4] has discussed the effect of traces of heavy metals on the determination of sulphur by the methylene blue procedure. We found that when water distilled from copper was used in reagent preparation, low results were obtained for small amounts of sulphur. This interference can be eliminated by using de-ionised water rather than distilled water for all reagents. The effect of distilled water is shown in Table I.

TABLE I.—THE EFFECT OF DISTILLED WATER ON THE DETERMINATION OF SULPHUR

	Concentration of sulphur, *ppm*	
Sample No.	De-ionised water	Distilled water
356-299	2·6	0·3
8228-172-3	3·4, 3·3	1·1
8238-166-T	1·7	0·4, 0·4
379-295-8	3·1, 2·6	1·4

Accuracy

In the absence of satisfactory iron standards in the low sulphur range, an evaluation of the accuracy of the methylene blue method was made with the help of radiochemical measurements. An iron-base alloy was strip-annealed until it was virtually sulphur free. It was then treated with iron sulphide containing ^{35}S and annealed to ensure homogeneity. This master sample was analysed for sulphur by the methylene

blue technique, and in addition the specific activity was measured. Portions of the master sample were then strip-annealed under varying conditions to produce samples containing different concentrations of sulphur. By measuring the specific activity of the annealed samples, a totally independent check of the chemical method of analysis was made. Results are given in Table II.

TABLE II.—A COMPARISON OF SULPHUR RESULTS BY RADIOCHEMICAL AND METHYLENE BLUE METHODS

	Concentration of sulphur, *ppm*	
Sample No.	Radiochemical	Methylene blue
Master alloy		21·4*
A	3·4	3·9, 3·8
B	6·1	6·1, 6·0
C	1·0	1·5, 1·5
X	0·29	0·48, 0·24, 0·38, 0·20, 0·27, 0·34
Y	0·07	0·39, 0·25

* This value was checked to within 1 ppm by combustion analysis.

The correlation coefficient between the two methods in Table II is 1·04, with a 95% Confidence Interval of 0·97–1·10 assuming no error in the radiochemical measurements. The actual confidence interval may be a bit larger since duplicate radiochemical determinations differed by about 10%.

Precision

Replicate results for a number of samples of iron-base alloys and manganese were obtained in order to ascertain the precision of the methylene blue method for sulphur when applied to these materials. Many of the samples were analysed by two chemists using different sets of apparatus in different laboratories. In most cases duplicate determinations were made on two or more days. Representative results are given in Table III.

TABLE III.—THE DETERMINATION OF SULPHUR IN MANGANESE AND IRON ALLOYS BY METHYLENE BLUE METHOD

Sample	Concentration of sulphur, *ppm*	
Manganese-2	230, 225	
Manganese-1	132, 142	
Iron-2	23·8, 21·6, 20·2, 19·2, 21·9, 22·7	s = 1·7
Iron-5	11·1, 10·9, 11·1	
Iron-8	3·4, 3·4	
Iron-ASTM-No. G	Analyst A 0·9, 0·7, 0·8, 0·9, 0·9	s = 0·1
	Analyst B 0·7, 1·0, 0·9, 0·8, 0·8	

Acknowledgements—Dr. Alex Goldman provided the doped iron-base alloys used in the accuracy study of this method. He also made most of the radiochemical measurements reported in this paper. Mr. Robert Pristera did many of the chemical analyses reported in Table I and Table III. The statistical work was done by Dr. Douglas Shaffer.

Zusammenfassung—Schwefel in Eisenlegierungen wird bestimmt durch Entwicklung von Schwefelwasserstoff. Letzterer wird mit N,N-dimethyl-p-phenylendiamin und Ferriion zur Reaktion gebracht und das gebildete Methylenblau spektrophotometrisch gemessen. Resultate für Schwefelgehalte von 0·3 bis 230 p.p.m. in säurelöslichen Metallproben werden mitgeteilt. Die Genauigkeit der Methylenblaumethode wurde mittels einer Radiotracertechnik überprüft.

Résumé—Les auteurs dosent le soufre dans les alliages de fer par dégagement à l'état d'acide sulfhydrique, suivi d'une réaction avec la N,N-diméthyl-p-phénylènediamine et le fer ferrique pour former le bleu de méthylène; ce dernier est déterminé par spectrophotométrie. Des résultats sont donnés pour des échantillons métalliques solubles dans les acides contenant 0,3 à 230 p.p.m. de soufre. Les auteurs ont évalué la précision de la méthode à l'aide de traceurs radioactifs.

REFERENCES

[1] L. H. Almy, *J. Amer. Chem. Soc.*, 1925, **47,** 1381.
[2] E. Fischer, *Ber.*, 1883, **16,** 2234.
[3] J. K. Fogo and M. Popowsky, *Analyt. Chem.*, 1949, **21,** 732.
[4] L. Gustafsson, *Talanta*, 1960, **4,** 227.
[5] *Idem., ibid.*, 236.
[6] W. Mecklenburg and F. Rosenkränzer, *Z. anorg. Chem.*, 1914, **86,** 143.

Talanta, 1962, Vol. 9, pp. 679 to 687. Pergamon Press Ltd. Printed in Northern Ireland

TITRIMETRIC ANALYSIS WITH CHLORAMINE-T—VIII*

THE CHLORAMINE-T—THALLIUM^{I} AND —THIOCYANATE REACTIONS AND SOME FURTHER APPLICATIONS EMPLOYING EXCESS OF REAGENT

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Summary—Direct oxidation of thallium^{I} in chloride or bromide media at acid concentrations of 0.05 to 3.0*M* is too slow to permit the use of visual indicators, and potentiometric titration reveals large positive errors. Double excess back titration following oxidation in acid chloride or bromide media gives excellent results provided the excess of oxidant is limited to 0·5 ml; oxidation in the absence of bromide is preferred. No satisfactory procedure for the determination of thiocyanate other than that previously advocated[4] could be devised. Reactions with hydrazine and thiosulphate give poor results, oxidation of nitrite is unsatisfactory, and hydroxylamine and vanadium^{IV} are not oxidised.

Examples of reactions involving excess of oxidant have been examined. Determination of sulphite in which chloramine-T is used quantitatively to liberate an excess of iodine is satisfactory. Determination of 8-hydroxyquinoline and of metals precipitated as oxinates by double excess back titration in which chloramine-T is used for the quantitative generation of bromine affords excellent results. Hexacyanoferrate(II) cannot be directly titrated, but determination by double excess back titration is possible, although the results are of poor accuracy.

DIRECT titrations with chloramine-T of thallium^{I} in "dilute" hydrochloric acid in the presence of "excess" potassium bromide using methyl orange as indicator,[2] and in 0·07 to 0·7*M* hydrochloric acid in a bromide concentration of 1·4*M* by the potentiometric method[3] have been reported. A precision of about 1 % was achieved. Titration in 3–5*M* hydrochloric acid with the aid of iodine monochloride as a reaction intermediate has already been scrutinised.[4] Titration in iodide media is not possible, because thallium^{III} oxidises iodide. Reactions in chloride and bromide media have been critically examined, and reaction conditions established in the present study.

Thiocyanate has been determined with chloramine-T by the tedious and rather imprecise method of addition of an excess of reagent to the thiocyanate in bicarbonate buffer, standing for 4 hr, addition of excess iodide, acidification with hydrochloric acid, and titration of the liberated iodine with thiosulphate.[5] Thiocyanate has also been titrated potentiometrically in neutral or dilute boric acid solution at an elevated temperature.[6] A careful examination of the titration in 3–5*M* hydrochloric acid using iodine monochloride as a reaction intermediate has already been reported.[4] This gives excellent and highly accurate results, and is the only satisfactory method for determination of thiocyanate with chloramine-T.

* For Part VII see reference 1.

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A considerable number of other reactions have been critically examined during the course of the present investigation. In many cases chloramine-T has proved convenient and accurate in use, and three typical examples of different modes of employment are given in illustration: one (sulphite) wherein chloramine-T is used for quantitative generation of iodine which is the active oxidant; one (oxine) of quantitative bromination in which chloramine-T is substituted for bromate; and one [hexacyanoferrate(II)] using chloramine-T as a substitute for cerium^{IV}. In others, *e.g.* hydroquinone, iron^{II}, no significant advance on previous work can be offered. The investigation of the iron^{II} reaction, for instance, substantially confirms the work of Poethke and Wolf.[7]

Certain reactions proved unprofitable.[8] Hydrazine gives inaccurate and unreproducible results,[1] though the reaction is utilisable in routine analysis. A similar marked divergence from the behaviour of bromate occurs in the failure of chloramine-T to oxidise hydroxylamine in bromide media even with the aid of molybdenum catalysts. Nor does chloramine-T oxidise vanadium^{IV}, although it will oxidise vanadium^{III}. The reaction with nitrite is unsatisfactory. Although under suitable conditions chloramine-T oxidises thiosulphate substantially to sulphate, and the reaction, like that with hydrazine, can be employed in routine work,[9] a side reaction producing the oxidation resistant tetrathionate ion results in a reaction deficiency of about 2%,[10,11] causing errors of about 0·2 to 0·5%. The oxidation of xanthate sulphur to sulphate, and the determination of xanthates and through them carbon disulphide, is likewise of a lower order of precision,[12] but has been found useful in agreement with Murthy's claims.[13,14]

EXPERIMENTAL

Apparatus and Reagents

The preparation and standardisation of solutions of chloramine-T,[15] arsenic^{III},[15] thallium^{I} [4] and thiocyanate[4] have been described. Indicators[16] and other reagents[17] and the quantitative and titrimetric apparatus and reagents[15] have been specified. The following reagents are additional to those previously used.

8-hydroxyquinoline: A 0·025*M* solution was prepared by dissolving 7·258 g of the AnalaR solid in 10 ml of AnalaR hydrochloric acid and dilution to 2 litres. The solution was standardised against primary standard 0·01667*M* potassium bromate.[18,19] A 10–20% excess of bromate solution is added to a 20-ml aliquot of oxine solution in a titration bottle to which has been added 10 ml of 1·0*M* potassium bromide and 10 ml of hydrochloric acid. After thorough mixing, a 10-ml aliquot of primary standard 0·05*M* arsenic^{III} solution is added and the excess back titrated with bromate using 1 ml of 0·1% α-naphthoflavone[18] or 0·3 ml of 0·1% rosaniline hydrochloride[19] as indicator (factor: 0·9987, 0·9997, 0·9990).

Potassium hexacyanoferrate(II): A 0·1*M* solution was prepared from the AnalaR trihydrate in water containing 0·04% of AnalaR sodium carbonate, and standardised by titration in 0·5*M* sulphuric acid with standard 0·1*M* cerate^{IV} solution using *o*-phenanthroline-iron^{II} sulphate as indicator[20] (factor: 1·1096, 1·110, 1·110).

Cerium^{IV}: An approximately 0·1*M* solution prepared from AnalaR ammonium hexanitratocerate (IV) in 0·5*M* sulphuric acid by the method of Smith,[21] and standardised against primary standard 0·05*M* arsenic^{III} solution in 0·5*M* sulphuric acid using osmic acid (3 drops of 0·01*M*) as catalyst and *o*-phenanthroline-iron^{II} sulphate as indicator.[22]

Sodium sulphite: An approximately 0·03*M* solution prepared from the AnalaR heptahydrate. The solution was standardised against primary standard 0·025*M* potassium iodate through 0·1*M* thiosulphate standardised[15] against the same iodate solution. An aliquot of the iodate solution is treated with an excess of iodide and acidified to 2·0*M* with hydrochloric acid. An aliquot of the sulphite solution is pipetted into this solution, and the excess iodine back titrated with thiosulphate[23] (factor: 0·0303, 0·0303, 0·0303).

Procedure

The techniques of potentiometric[15,17] and visual indicator[15] titration have been described. For thallium and thiocyanate equivalence point volumes of 200 ml for potentiometric and 100 ml for

visual indicator titrations were used, due allowance being made for washings, and the concentrations specified are referred to the equivalence point. Details of the other techniques are as follows.

Double excess back titration

This technique has been mentioned[15,17] and employed in various titrimetric processes.[8,19] It is useful for reactions which are too slow to allow direct titration, but which can be made quantitative by the use of an excess of the initial titrant. It consists in the addition of an excess of the initial titrant *A* followed after the appropriate reaction interval by an excess of a second reagent *B* and titration of the second excess by means of the initial titrant *A*. Reagent *B* is chosen to react rapidly and so be directly titratable with *A*. This has the advantages of employing only one standard solution, of a single filling of a single burette with *A*, and of allowing the addition of a regulated amount of *A*, such as 23 or 27 ml which is not readily measurable by pipette, and which, moreover, need not be accurately measured because the same burette-full is to be used in completing the titration. If the standard solution is *A*, then the titre of the amount of *B* added can be determined by blank titration of an amount of *B* similar to that used in the determination; when *B* is also a standard solution, the titre may be calculated directly. The consumption of *A* by the substance to be determined is calculated by subtraction of the titre of *B* from the total consumption of *A*. If the standard solution is *B*, then a similar process affords a standardisation of *A* contiguous with the determination, a process occasionally convenient for use with titrants of poor stability.

This technique has frequently been of value with chloramine-T and is illustrated in the determination of thallium[I], 8-hydroxyquinoline and metal oxinates [method (a)] and hexacyanoferrate(II). Single excess back titration is illustrated in the determination of sulphite and 8-hydroxyquinoline [method (b)].

Determination of sulphite

Transfer to a titration bottle an aliquot of standard chloramine-T solution equivalent to about twice the amount of sulphite to be determined. Add 100 ml of water, 5 ml of 2*M* hydrochloric acid and 1 g of potassium iodide. Add an aliquot of the sulphite solution (discharge of the pipette in the normal fashion caused no significant error, so that delivery of the solution with the pipette tip immersed in the iodine solution is unnecessary), stopper the bottle, shake and allow to stand for 1 min. Remove and rinse the stopper, and titrate the excess iodine with standard thiosulphate solution, adding 2 ml of 1% starch solution as indicator near the end-point.

Determination of 8-hydroxyquinoline

Transfer to a titration bottle an aliquot of oxine solution (20 ml of 0·025*M*) or a solution of the metal oxinate precipitate in hydrochloric acid. Add 10 ml of 10*M* hydrochloric acid (less the amount used to dissolve the precipitate) and 1 g of potassium bromide. Add from a burette a 15% excess (23 ml) of standard chloramine-T, stopper the bottle, shake and allow to stand for 5 min. Determine the excess of bromine by either of the following methods:

(a) *Double excess back titration.* Add an excess (10 ml of 0·05*M*) of standard arsenic[III] solution and a further 5 ml of 10*M* hydrochloric acid. Titrate the excess arsenic[III] with the chloramine-T remaining in the burette. Use 1 ml of 0·1% α-naphthoflavone added about 1 ml before the equivalence point, or 0·2 ml of 0·1% *p*-ethoxychrysoïdine as indicator. Determine the arsenic blank under the same conditions.

(b) *Single excess back titration with thiosulphate.* Add 2 g of potassium iodide and back titrate the liberated iodine with standard thiosulphate solution using starch as indicator.

Determination of hexacyanoferrate(II)

Double excess back titration with chloramine-T and arsenic[III]. Transfer an aliquot (20 ml of 0·1*M*) of hexacyanoferrate(II) solution to a titration bottle, add 2 ml of 2*M* hydrochloric acid and run in a 50% excess (30 ml of 0·05*M*) of standard chloramine-T solution from a burette. Stopper, shake and allow to stand for 10 min. Add an aliquot of standard arsenic[III] solution in excess of the excess of oxidant, 15 ml of 10*M* hydrochloric acid and 1 g of potassium bromide. Titrate the excess of arsenic[III] with the chloramine-T remaining in the burette, using 0·2 ml of 0·1% methyl orange added 1 ml before the equivalence point as indicator. Determine the arsenic blank under the same conditions.

RESULTS AND DISCUSSION

Determination of thallium[I]

Thallium[I] may be accurately determined by titration with bromate[24] in a hydrochloric acid medium with or without the addition of bromide or by the Andrews procedure with iodate.[25,26] In the presence of chloride or bromide, thallium[I] chloride

or bromide is precipitated and reacts only slowly with chloramine-T. The use of colour indicators such as methyl orange[2] and bordeaux has, therefore, proved impracticable in direct titration. Potentiometric titration has been investigated under a variety of conditions.

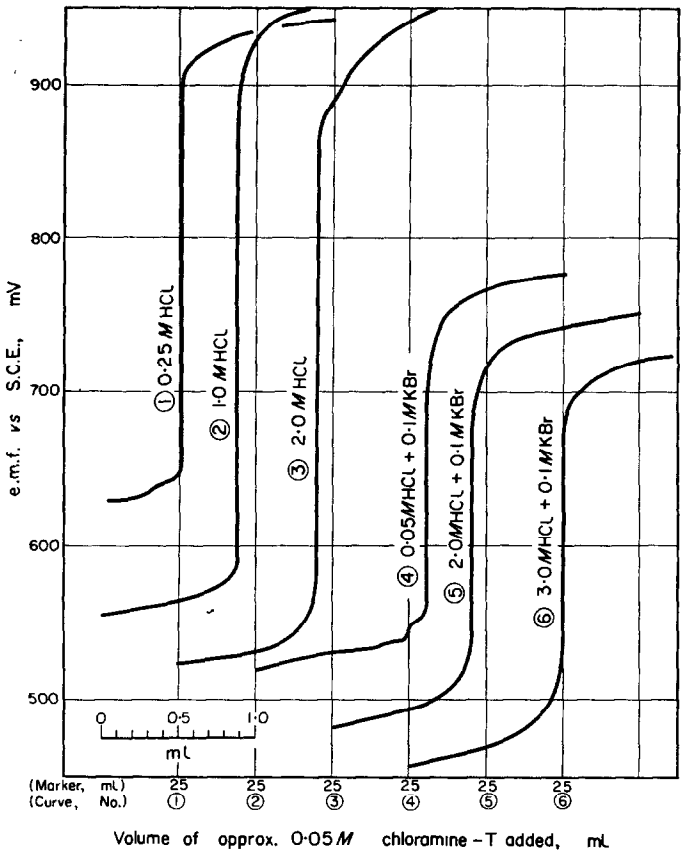


FIG. 1.—Direct titration of 25-ml aliquots of approx. $5 \times 10^{-2}M$ thallium[1] at an equivalence point volume of 200 ml, with approx. $5 \times 10^{-2}M$ chloramine-T.

TABLE I—POTENTIOMETRIC TITRATION OF THALLIUM[1] WITH CHLORAMINE-T IN VARIOUS MEDIA

Concentration, *M* HCl	KBr	End-point, *ml*	Error %
0·25	—	25·02	+0·81
1·0	—	24·87	+0·20
2·0	—	24·89	+0·28
0·05	0·1	25·12	+1·21
2·0	0·1	24·91	+0·36
3·0	0·1	24·98	+0·65

Calculated equivalence point: 24·82 ml.

(a) *Potentiometric titration in hydrochloric acid.* The curves are shown in Fig. 1, and give large and sharp breaks in potential, but the results given in Table I are all high. The reaction was slow in all titrations, though the potentials were steady in 1 and 2*M* acid before the end-point. In 0·25*M* acid the potentials were unstable. After the end-point in all titrations the potentials became steady.

(b) *Potentiometric titration in hydrochloric acid containing potassium bromide.* The effect of an equivalence point concentration of 0·1*M* bromide was examined at hydrochloric acid concentrations from 0·05 to 3·0*M*.

In acid concentrations of 0·05 to 1·0*M*, the reaction was too slow to be analytically useful. However, since reaction at low acid concentrations has been advocated,[3] a titration was conducted in 0·05*M* acid, in which the chloramine-T was added rapidly up to within 1 ml of equivalence, ignoring the production of a large temporary excess of volatile bromine which slowly reacted with the precipitate. The accuracy attained by this method was comparable to that previously claimed,[3] but was inferior to that achieved in higher acid concentrations. In 2–3*M* acid the reaction was sufficiently fast to permit titration in the normal manner. The potential changes are large and sharp (Fig. 1), but the results are still high. Potentials were steady before the end-point and equilibrated rapidly thereafter.

Direct titration in hydrochloric acid solution, with or without the addition of bromide, is subject to errors of at least +0·2% and cannot, therefore, be recommended.

Determination with chloramine-T by the Andrews procedure has, however, proved to give excellent results,[4] under the proper conditions.

Since direct titration proved inaccurate, oxidation with excess of chloramine-T followed by determination of the excess of oxidant and hence the net consumption of oxidant by thallium[I] was examined under a variety of conditions by the double excess back titration method (*vide supra*). Oxidations in the presence and absence of bromide were compared and the amount of excess oxidant, the acid concentration and the time of oxidation were investigated.

(c) *Oxidation in hydrochloric acid.* A variable amount of 10*M* hydrochloric acid with water to make an oxidation volume of 100 ml was added to an aliquot of the thallium solution in a titration bottle followed by a variable excess of chloramine-T, the bottle stoppered, shaken and allowed to stand for 1–5 min. Then 10 ml of standard arsenic[III] solution and 10 ml of 1*M* potassium bromide were added and the titration completed in an equivalence point volume of 150 ml with chloramine-T using rosaniline as indicator.[15,16] The results in Table II indicate that in 1–2*M* acid, with an excess of 0·5–1·0 ml of oxidant and a reaction time of 1 min or more, the method gives errors of less than 0·1%, which is as good as the preferred method.[4]

(d) *Oxidation in hydrochloric acid at a bromide concentration of* 0·1*M*. The method is similar to the previous one, except that the bromide (10 ml of 1·0*M*) is added along with the hydrochloric acid. With an excess of 0·3 to 0·5 ml of oxidant in 1–2*M* acid and a reaction time of at least 1 min, the results (Table II) are equally as good as the previous ones, but with a greater excess of oxidant, the positive errors increase rapidly.

The double excess back titration procedure is, therefore, capable of giving results of an accuracy of 0·05%, and is recommended for this determination. Though there is little to choose between the alternative methods under the proper conditions, initial oxidation in the absence of bromide is preferred. This reaction affords yet

another instance of the failure of chloramine-T as a substitute for bromate in direct titration.[15,24]

Determination of thiocyanate

Though it is possible that the methods noticed above involving prolonged action of excess oxidant in bicarbonate buffer[5] or potentiometric titration at elevated temperature[6] may give acceptable results, neither is convenient. Attempted titrations with chloramine-T in hydrochloric acid of various concentrations, with or without the addition of bromide were unsuccessful because of the slowness of the reaction. Reaction with excess of oxidant under similar conditions followed by a double excess back titration or a single excess back titration were equally unsuccessful, with reaction times of up to 30 min. In view of the excellent results achieved in 3–5*M* hydrochloric acid in the presence of iodine monochloride for both potentiometric and visual indicator titrations with chloramine-T,[4] other methods were not pursued.

TABLE II—DETERMINATION OF THALLIUM^{I} WITH CHLORAMINE-T BY DOUBLE EXCESS BACK TITRATION

Excess of chloramine-T added, *ml*	Volume of 10*M* HCl used, *ml*	Period of standing, *min*	Total titration, *ml*	Chloramine-T equivalent to Tl^{I}, *ml*	Error %
Method (a)					
0·5	10	1	34·83	24·83	+0·04
0·5	10	5	34·84	24·84	+0·08
1·0	10	1	34·84	24·84	+0·08
0·5	20	1	34·83	24·83	+0·04
0·7	15	3	34·83	24·83	+0·04
Method (b)					
0·3	10	1	34·83	24·83	+0·04
0·5	10	1	34·84	24·84	+0·08
0·5	10	5	34·84	24·84	+0·08
0·5	20	1	34·83	24·83	+0·04
0·8	10	1	34·86	24·86	+0·16
1·0	10	1	34·88	24·88	+0·24

Chloramine-T titre of arsenic^{III} solution added: 10·0 ml; calculated total titration volume: 34·82; calculated titre of thallium^{I} solution: 24·82 ml.

Determination of sulphite

It is not possible to determine sulphite by direct titration in acid solution because both the volatility of sulphur dioxide and the direct and induced air oxidation of sulphite lead to low results. Chloramine-T proved no exception. Similar errors in lesser degree arise on rapid addition of excess oxidant to the sulphite solution prior to back titration of the excess. Errors are minimised by the addition of the neutral sulphite to an excess of oxidant, acidified if necessary before or after the addition.

Such a method proved very satisfactory with chloramine-T, used to liberate an excess of iodine from an acidified iodide solution, the excess being back titrated with thiosulphate as described above. The results for the factor of a sulphite solution (0·0303, 0·0303, 0·0303*M*) compare favourably with the parallel method[23] using standard iodate.

Determination of 8-hydroxyquinoline and of metal oxinates

The use of standard bromate quantitatively to generate known amounts of free bromine from acidified bromide solutions for the quantitative bromination of aromatic amino and hydroxy compounds is well known. The use of chloramine-T as a replacement for bromate in similar reactions has been investigated and has been found successful. The conditions and procedure are similar to those employed for

TABLE III—TITRATION OF 8-HYDROXYQUINOLINE WITH CHLORAMINE-T

Method	Indicator	Factor	Error, %
(a)	α-naphthoflavone	1·000	+0·09
(a)	*p*-ethoxychrysoïdine	0·9995	+0·04
		1·0005	+0·14
(b)	starch	1·000	+0·09
		1·000	+0·09
		1·001	+0·19
		1·000	+0·09

Factor of the 0·025*M* 8-hydroxyquinoline by bromate titration: 0·9991.

TABLE IV—DETERMINATION* OF METALS BY PRECIPITATION OF THE METAL OXINATE FOLLOWED BY TITRATION OF THE OXINE BY METHOD (a) USING ROSANILINE AS INDICATOR

Metal	Taken, *mg*	Found, *mg*	Error, %
Zn	16·00	15·91	−0·56
	16·00	15·93	−0·44
	4·00	4·01	+0·25
	4·00	4·02	+0·50
Co	15·00	14·96	−0·27
	15·00	15·06	+0·40
	3·75	3·78	+0·80
	3·75	3·76	+0·27
Al	4·50	4·56	+1·33
	4·50	4·51	+0·22
	1·125	1·13	+0·44
	1·125	1·12	−0·44

* Determinations made by first year undergraduate students in E.B.'s laboratories.

bromate. As an example, the doubly useful determination of oxine and its metal complexes is given in illustration.

Bromination of oxine proved to be too slow to permit direct titration, even with the reversible indicator α-naphthoflavone, so that a double excess back titration procedure [method (a) above] using arsenic^{III} to remove the initial excess of bromine,[19] and a single excess procedure [method (b) above] using iodide and thiosulphate were examined. Both methods give excellent results in good agreement with the bromate results, as shown in Table III.

A number of metals were precipitated as oxinates by established procedures, the washed precipitates dissolved in hydrochloric acid and the equivalent oxine titrated

by method (a) using rosaniline as indicator for the final titration. The results obtained by undergraduate students were satisfactory as shown in Table IV.

Oxine and its metal complexes can, therefore, be determined accurately by bromination using chloramine-T in place of bromate. A preference for the double excess back titration procedure is expressed.

Determination of hexacyanoferrate(II)

Again, direct titration proved to be too slow to permit the use of visual indicators, so that the double excess back titration procedure was investigated. By the method described above, values for the factor of a 0·1*M* hexacyanoferrate(II) solution of 1·105, 1·105 and 1·105 were obtained, showing an error of −0·5% with respect to the figures given by direct titration with cerium^{IV}. Though the reproducibility (precision) is good, the accuracy is poor, and the method has little to recommend it other than economy in the expense of the reagent used.

Zusammenfassung—Die direkte Oxydation von Thallium(I) in chlorid- oder bromidhaltiger Lösung bei Säurekonzentration von 0·05 bis 3·0 m ist zu langsam um die Verwendung visueller Indicatoren zu gestatten und die potentiometrische Anzeige gibt stark positive Fehler. Eine der Oxydation folgende doppelte Rücktitration gibt ausgezeichnete Ergebnisse, wenn darauf geachtet wird, dass der Überschuss an Oxydans 0·5 ml nicht überschreitet; Oxydation in Abwesenheit von Bromid wird vorgezogen. Keine andere Methode zur Bestimmung von Thiocyanate als die bereits früher vorgeschlagene[4] kann empfohlen werden. Die Reaktion mit Hydrazin und Thiosulfat gibt schlechte Resultate, die Oxydation von Nitrit verläuft nicht zufriedenstellend und Hydroxylamin und Vanadin(IV) werden nicht oxydiert.

Beispiele, bei denen Überschuss an Oxydans angewendet wurde, wurden studiert. Die Bestimmung von Sulfit, bei der Chloramin-T angewandt wird um quantitativ einen Überschuss von Jod zu erzeugen, verläuft zufriedenstellend. Die Bestimmung von Metallen über ihre Oxinate mittels doppelter Rücktitration gibt hervorragende Resultate (Chloramin T wird zur quantitativen Erzeugung von Brom verwendet). Ferrocyanid kann nicht direkt titriert werden. Bestimmung mittels doppelter Rücktitration ist möglich, doch sind die Resultate nicht sonderlich gut.

Résumé—L'oxydation directe du thallium(I) en milieu chlorure ou bromure à des concentrations d'acide de 0,05 à 3,0 M est trop lente pour permettre l'utilisation d'indicateurs visuels, et le titrage potentiométrique révèle de grandes erreurs positives. Le titrage en retour d'un double excès suivant l'oxydation en milieu acide, chlorure ou bromure donne d'excellents résultats à condition que l'excès d'oxydant soit limité à 0,5 ml; l'oxydation en l'absence de bromure est préférée. Aucune méthode satisfaisante, pour le dosage du thiocyanate, autre que celle qui a été recommandée antérieurement (4) ne pourrait être imaginée. Les réactions avec l'hydrazine et le thiosulfate donnent de mauvais résultats, l'oxydation du nitrite n'est pas satisfaisante, l'hydroxylamine et le vanadium(IV) ne sont pas oxydés.

Des exemples de réactions mettant en jeu un excès d'oxydant ont été examinés. Le dosage du sulfite, dans lequel la chloramine T est utilisée pour libérer quantitativement un excès d'iode, est satisfaisant. Le dosage de 8-hydroxyquinoléine et de métaux précipités à l'état d'oxinates, par titrage en retour d'un double excès, dans lequel la chloramine T est utilisée pour la production quantitative de brome, donne d'excellents résultats. Le ferrocyanure ne peut être titré directement, mais le dosage par titrage en retour est possible, bien que les résultats aient une mauvaise précision.

REFERENCES

[1] E. Bishop and V. J. Jennings, *Talanta*, 1962, **9**, 603.
[2] A. J. Berry, *Analyst*, 1934, **55**, 736.
[3] C. del Fresno and A. Aguado, *Z. analyt. Chem.*, 1937, **109**, 334.
[4] E. Bishop and V. J. Jennings, *Talanta*, 1962, **9**, 581.
[5] A. S. Komarovsky, W. F. Filanova and I. M. Korenman, *Z. analyt. Chem.*, 1934, **96**, 321.
[6] B. Samek, *Chem. Zentr.*, 1942, **1**, 517.
[7] W. Poethke and F. Wolf, *Z. anorg. Chem.*, 1952, **268**, 244.
[8] V. J. Jennings, *Titrimetric analysis with chloramine-T*. Univ. Exon., 1957.
[9] A. R. V. Murthy, *Current Sci.*, 1953, **22**, 342.
[10] E. Bishop and V. J. Jennings, *Talanta*, 1961, **8**, 697.
[11] A. R. V. Murthy, private communication, 1960.
[12] E. Bishop and G. D. Short, unpublished work.
[13] V. R. S. Rao and A. R. V. Murthy, *Talanta*, 1960, **4**, 206.
[14] S. R. Rao, *ibid.*, 1961, **8**, 746.
[15] E. Bishop and V. J. Jennings, *ibid.*, 1958, **1**, 197.
[16] *Idem*, *ibid.*, 1961, **8**, 34.
[17] *Idem*, *ibid.*, 1961, **8**, 22.
[18] R. Belcher, *Analyt. Chim. Acta*, 1949, **3**, 578.
[19] E. Bishop, *A course of elementary quantitative analysis*. University of Durham, 1946.
[20] I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*. The Macmillan Co., New York, 3rd Ed., 1952, p. 583.
[21] G. F. Smith, *Cerate Oxidimetry*. G. F. Smith Chemical Co, Columbus, Ohio, U.S.A., 1942, p 13.
[22] K. Gleu, *Z. analyt. Chem.*, 1933, **95**, 205.
[23] W. S. Hendrixson, *J. Amer. Chem. Soc.*, 1925, **47**, 2159.
[24] E. Bishop, *Analyst*, 1958, **83**, 212; *Mikrochim. Acta*, 1956, 619.
[25] G. F. Smith and C. S. Willcox, *Ind. Eng. Chem., Analyt.*, 1942, **14**, 49.
[26] E. H. Swift and C. S. Garner, *J. Amer. Chem. Soc.*, 1936, **58**, 113.

Talanta, 1962, Vol. 9, pp. 689 to 697. Pergamon Press Ltd. Printed in Northern Ireland

STUDIES ON URONIC ACID MATERIALS—V*

THE THERMAL DECARBOXYLATION METHOD OF ANALYSIS

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Summary—The thermal decarboxylation method of determining uronic acids, proposed by Perlin, has been investigated. A specially designed oven, having good temperature stability, enabled the thermal decomposition of various compounds to be studied kinetically, with good reproducibility. Comparatively large errors can arise in the determination of the carbon dioxide evolved; these errors originate in the nature of the other volatile reaction products. Typical results are presented, and it is concluded that thermal decarboxylation does not compare favourably with the 150-min acid decarboxylation as a general analytical method.

VARIOUS aspects of the acid decarboxylation of uronic acid groups have been investigated[1,2,3] in attempts to improve the accuracy and reliability of this analytical reaction,[4] which is important in carbohydrate chemistry. The formation of potentially acidic vapours, such as methyl chloride and methyl formate, gives a source of error; a knowledge of these products is also important in studies of the reaction mechanism. A comprehensive study[5] was therefore made of the volatile reaction products from some 80 carbohydrate materials and related compounds: a vapour-phase infrared method[6] showed that the products included furan, 2-methylfuran, acetone, methylethylketone, diethylketone, acetaldehyde, propionaldehyde, chloral, methyl formate, methyl chloride and dimethylformal, although not all of these are formed from any one sugar residue. Acetone was known to be an acid decomposition product of rhamnose[7] and other sugars,[8] but the formation of some of the other compounds was unexpected. They have, however, been found subsequently[9] as products of the thermal decomposition of various carbohydrate materials. Under other experimental conditions the formation of other volatiles has also been reported, *e.g.*, methyl glyoxal, acetol and diacetyl from reducing sugars,[10] maltol and isomaltol[11] from the pyrolysis of starch.

There have been many studies of the formation of pyrodextrins[12,13] and the production of volatile organic compounds during thermal decomposition is, of course, well known[14] (*cf.* ref. 9). This formation of organic vapours by chemical reaction must be distinguished from the desorption of physically retained organic solvents. Although the latter effect has long been recognised,[15] and further examples continue to be reported,[16] it is now known[17] that solvent-retention continues up to the temperature at which the carbohydrate concerned begins to decompose. A knowledge of the pretreatment of the sample is therefore important in thermal decomposition studies.

Differential thermal analysis has been applied to starches[18] and other polysaccharides;[19] it has been suggested that decarboxylation causes a small endothermic

*Part IV: D. M. W. Anderson, A. M. Bews, S. Garbutt and N. J. King, *J. Chem. Soc.*, 1961, 5230.

reaction observed for uronic acid materials at 145–155°. Although these temperatures are only slightly higher than those at which carbohydrate decomposition was observed to begin,[17] they are some 100° lower than the decomposition temperatures proposed for the thermal decarboxylation method[20] of estimating uronic acids.

Since it appeared that Perlin's method[20] has not been widely adopted or studied further (*cf.* ref. 20), an examination of its applicability appeared to be a logical extension of our studies. This paper presents some results which show that thermal decarboxylation is inferior, for several practical reasons, to the acid decarboxylation reaction as a quantitative method[2,3] for the analysis of uronic acid contents.

EXPERIMENTAL

Design of apparatus

In Perlin's experiments,[20] the method of heating involved the refluxing of vapours. Whilst this method offers the advantage that over-heating cannot possibly occur, it is restrictive, since a continuous range of temperatures cannot be studied. Moreover, the absolute reaction temperature could not be established:[20] the reaction conditions are critical[18] in this type of investigation.

Preliminary investigations[5] revealed that careful experimental design would be required to give minimum temperature equilibration times with run-to-run reproducibility at absolute temperatures. Successive refinements with different designs of apparatus showed that, after the required stability of oven temperature was achieved, the following factors were also critical: (*a*) stabilisation of rate of flow-gas, (*b*) pre-heating of flow-gas to the required reaction temperature, (*c*) reproducible location of samples at the same position within the oven, (*d*) measurement of the actual sample temperature during the decomposition.

The apparatus finally satisfying all these requirements is represented diagramatically in Fig. 1. With its use, the rate of decomposition of a particular sample was reproducible to within ±2%.

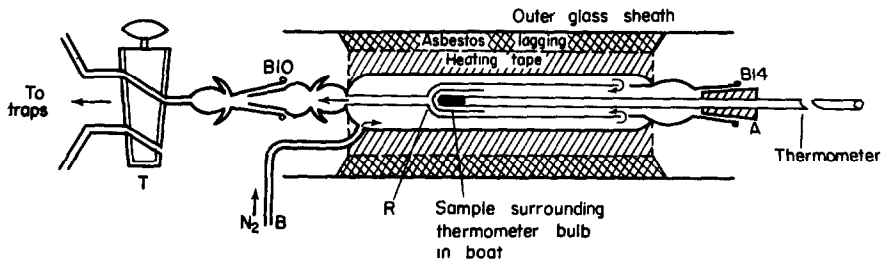


FIG. 1.—Construction of thermal decomposition apparatus.

Constructional details: The internal dimensions are a function of the size and shape of the sample-boat which, in turn, is dictated by the weight of sample necessary for the production of suitable quantities of carbon dioxide. Suitable sample weights were 30 mg for uronic acids and polyuronides, 100 mg for non-uronides. The boat must be sufficiently deep to contain the increased volume occupied by the samples upon decomposition: porcelain boats, 35 × 12 × 6 mm, were suitable.

By grinding off one end (the "hook" end) of a boat, a form of long-handled weighing-spoon was made, with a thermometer, bound to the boat by several turns of platinum wire, acting as the handle: samples were added carefully so as to surround the mercury bulb. A tightly-fitting rubber stopper was positioned on the thermometer stem at a part of the scale where readings were not required. The position chosen dictated the effective length of the "weighing spoon" handle; the constriction in the bore of the oven was positioned during manufacture so as to provide a locating device against which samples could be positioned centrally and reproducibly within the oven at its hottest part.

Heating: The external dimensions of the oven, 17 cm × 2.3 cm, were chosen so that its whole surface could be wound with a heating tape, 30″ long, 1″ broad ("Electrothermal" type HT 350). The heating tape was lagged with a layer of asbestos tape, and enclosed within an open-ended tightly-fitting glass sleeve, 25 cm long and 4 cm in diameter, which enclosed the whole assembly from A to B. Temperatures could be varied within the range 140–300° by adjustment of the Variac which supplied the continuous heating voltage. For particular temperatures, long- and short-period temperature variation did not exceed ±1° after several hours had been allowed for the establishment of equilibrium conditions.

Flow-gas: Cylinder nitrogen ("N.O.F." grade), dried and freed of traces of carbon dioxide by passage through scrubbing towers, was used. The flow-rate was established at 15 ml per min by means of two needle valves, a capillary-tube buffer system, and a calibrated Rotameter. For some experiments, residual traces of oxygen (approx. 20 ppm) in the cylinder gas were also removed by passage through a "Nilox" purifier (Southern Instruments Ltd.). Inclusion of the nitrogen inlet system within the jacketed heating assembly ensured that the flow-gas was correctly pre-heated.

Use of apparatus

Determination of the carbon dioxide evolved: Kinetic measurements were facilitated by a two-way stop-cock system and matched pairs of traps, as described.[21] Determinations were made (*a*) titrimetrically using a titration-cell designed[2] for carbon dioxide titrations, (*b*) gravimetrically, using conventional analytical adsorption tubes, (*c*) by infrared spectroscopy,[6] using the manometric calibration method.

Use of sulphuric acid bubblers: In some experiments, as indicated below, the gas-stream from the oven was led through a conventional gas-bubbler before determination of the carbon dioxide.

Detection of carbon monoxide: Standard colorimetric reactions[22] were used. The molybdenum blue method could not be used when sulphur dioxide was also present (*cf.* ref. 22, p. 347), and the palladous chloride method was therefore employed.

Identification of the volatile products: For each compound studied separate runs, using samples of 500 mg, were made so that the volatile products (before and after passage through the sulphuric acid bubbler) could be trapped in liquid nitrogen[23] and subsequently examined by the vapour-phase infrared technique.[6] (*Cf.* ref. 17).

Procedure: With the nitrogen flow-rate stabilised at 15 ml per min and with a thermometer-handled weighing-spoon in position, the oven temperature was allowed to equilibrate (usually overnight) at the required temperature. The weighing-spoon was withdrawn and allowed to cool, stop-cock T (Fig. 1) being closed so that the flow of nitrogen, emerging at A, prevented air from entering the oven. The sample, weighed by transfer from a suitable weighing-scoop, was added to the thermometer-spoon so as to surround the thermometer-bulb. The thermometer-spoon was replaced carefully in the oven, and stop-cock T opened. Preliminary experiments with water had established the internal volume (V ml) of the system from restriction R to T; V/15 min after opening T was taken as the zero-time for the kinetics. The sample reached the pre-established equilibrium temperature of the oven after about 5 min (*cf.* ref. 20). Thus results quoted below for "20 min at 255°" are, in effect, for 5 min heating over the range 0–255° + 15 min heating at 255°.

Origin of samples

The samples of glucurone and galacturonic acid monohydrate had 97% and 96% purity, respectively, by acid decarboxylation,[3] and have been described.[21] The alginic acid, pectic acid and pectin were commercial samples, for which acid decarboxylation[3] gave 79%, 61% and 57% respectively: the pectic acid and pectin contained 0.1% and 6.5%, of methoxyl, respectively. The sample of *Acacia seyal*[24] gum contained 12% of glucuronic acid, and 1% of methoxyl.

The non-uronic samples studied were of commercial origin and were chromatographically pure.

RESULTS AND DISCUSSION

1. *Uronic acids and polyuronides*

Fig. 2 (dotted curves) shows the results obtained titrimetrically for decomposition at 255°; for temperatures between 255° and 280° the initial rate of evolution of carbon dioxide was faster, but the curves levelled off more quickly, so that the total yields were not significantly greater. Above 280°, however, the decomposition mechanism apparently changes, since the yields of carbon dioxide were considerably increased. Thus, after decomposition for 1 hr at 300°, titrimetric determinations indicated apparent uronic acid contents of 96%, 107% and 87% for glucurone, galacturonic acid and alginic acid respectively.

The titrimetric values for the yield and rate of evolution of carbon dioxide at 255° were much less than were reported by Perlin.[20] The experiments were therefore repeated, the carbon dioxide being determined gravimetrically. The apparent yields of carbon dioxide, as shown in Fig. 2 (full lines) agreed much more closely with Perlin's

values, the acid decarboxylation values for galacturonic acid and alginic acid—but not for glucurone—now being attained in approx. 20 min. Reasons for the large discrepancy between the titrimetric and gravimetric results had therefore to be found.

Investigation of the volatile reaction products: Carbon monoxide was detected colorimetrically, in agreement with Perlin.[20] Vapour-phase infrared spectroscopy showed that, after removal of carbon dioxide and water, the volatile products included acetone and other carbonyl compounds. Although these were formed in considerable quantity (*cf.* Perlin's "distillable oils") they were evidently of low volatility and their identification lay outside the applicability of the vapour-phase spectroscopic method.

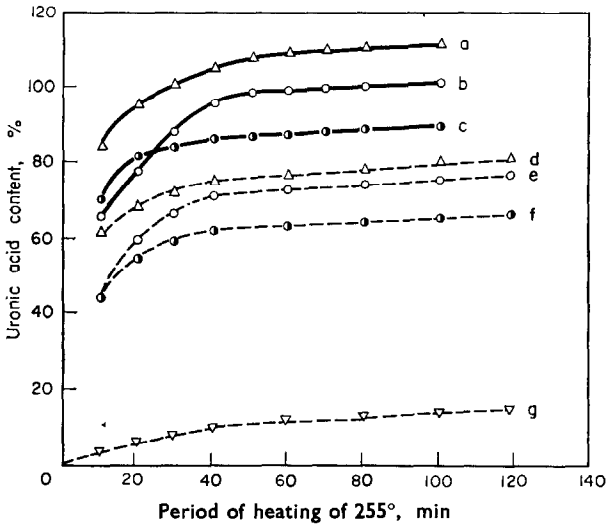


FIG. 2.—Rate of evolution of carbon dioxide from uronic compounds at 255°

Curve (*a*) galacturonic acid
(*b*) glucurone
(*c*) alginic acid
} gravimetric determination of carbon dioxide

Curve (*d*) galacturonic acid
(*e*) glucurone
(*f*) alginic acid
(*g*) *Acacia seyal* gum
} titrimetric detetermination of carbon dioxide

When these reaction products were passed through a sulphuric acid bubbler, spectroscopy showed that although the carbonyl compounds had been removed, sulphur dioxide and increased quantities of carbon monoxide, together with traces of carbon dioxide, were now present in the carrier-gas emerging from the bubbler. Evolution of these acidic gases continued for several hours after the end of a run. The thermal decomposition products must therefore include significant quantities of formic acid and other organic acids (*cf.* ref. 22, p. 347).

Infrared estimations of the amounts of carbon dioxide present in the mixture of acidic decomposition products indicated that direct titrimetric determinations gave the most reliable estimation of the actual carbon dioxide content. Titrimetric results are considerably higher if a sulphuric acid bubbler is used, as shown in Table I; the increased apparent uronic acid content results from the acidic gases evolved from the scrubber.

Fig. 1 also shows the corresponding figures for gravimetric determinations. Without a sulphuric acid bubbler, the result is virtually the total of all the volatile products: insertion of the bubbler gives lower results, which, however, are still high as a result of the acidic vapours released from the bubbler. A measure of these is given in Table I, column (*c*). When this is applied as a correction to column (*e*), the values expressed in columns (*a*) and (*f*) are, for experiments of this kind, in reasonable agreement with the estimations given by the specific infra-red method.

TABLE I. DEPENDENCE OF THE APPARENT PERCENTAGE URONIC ACID CONTENT ON THE METHOD OF ESTIMATING THE CARBON DIOXIDE EVOLVED*

Compound	Titrimetric			Gravimetric			Spectroscopic
	(*a*) Without H_2SO_4 scrubber	(*b*) With H_2SO_4 scrubber	(*c*) Difference (*b*–*a*)	(*d*) Without H_2SO_4 scrubber	(*e*) With H_2SO_4 scrubber	(*f*) Corrected Value (*e*–*c*)	
Glucurone	73	84	11	99	88	77	70–75
Galacturonic acid	77	91	14	109	97	83	75–80
Alginic acid	64	72	8	87	77	69	65–70

* All results quoted refer to decarboxylation at 255°for 1 hr.

TABLE II. APPARENT PERCENTAGE URONIC ACID CONTENT OF SOME SUGARS

Sugars	Thermal Decarboxylation at 255°				Decarboxylation in 19% HCl		
	30 min	60 min	90 min	120 min	50 min	100 min	150 min
Glucose	3·2	5·8	7·1	8·6	1·0	1·6	1·9
Galactose	2·5	5·8	6·2	8·4	1·4	2·2	2·9
Mannose	3·2	6·6	7·3	8·9	2·1	3·0	3·5
Arabinose	3·6	6·0	6·3	6·7	0·9	1·4	1·8
Xylose	4·7	6·6	8·5	9·7	1·1	1·4	1·6
Rhamnose	4·1	6·4	7·5	8·3	1·9	2·7	3·2
Fucose	5·2	6·7	7·4	8·2	1·2	2·1	2·8

TABLE III. APPARENT PERCENTAGE URONIC ACID CONTENT OF GLUCOSE ON THERMAL DECOMPOSITION AT DIFFERENT TEMPERATURES

Temp., °C	Period of heating, *min*			
	30	60	90	120
245	0·6	2·5	4·1	5·7
255	3·2	5·8	7·1	8·6
265	4·1	7·6	9·8	11·0

2. *Non-uronic, non-methylated sugars*

Direct titrimetric determinations of the carbon dioxide evolved at 255° gave the results shown in Table II. These results are similar to those reported by Perlin,[20] who found apparent uronic acid contents of "about 3% in 15 min" for reducing sugars.

When the values found are compared in Table II with values obtained by the 150-min acid decarboxylation method,[3] however, it is apparent that the thermal decomposition method gives relative errors which are considerably greater for most of the common sugars studied.

Temperature-dependence of the decomposition: Table III lists the results found by direct titration for glucose at 245°, 255° and 265°.

Volatile decomposition products other than carbon dioxide and water: (*a*) For glucose, galactose and mannose, only trace amounts of volatile products were formed, the main component being acetaldehyde. Gravimetric experiments, with and without sulphuric acid scrubbing, showed that the results were only marginally greater than those quoted in Table II.

(*b*) For arabinose, rhamnose and fucose, however, much larger amounts of acetaldehyde were formed, and gravimetric results were up to 50% higher than those

TABLE IV. COMPARISON OF THE APPARENT PERCENTAGE URONIC ACID CONTENTS OF METHYLATED COMPOUNDS AS FOUND BY DIFFERENT METHODS

Compound	Thermal decomposition for 1 hr at 255°			Decarboxylation for 2·5 hr in 19% HCl		Spectroscopy
	Volatile decompn. products	Titrimetric detn.	Grav. detn.	Volatile decompn. products	Titrimetric detn.	
2:3:4:6-tetra-*Q*-methyl glucose	carbon dioxide methyl formate	*	*	carbon dioxide methyl chloride	1·7	0·8
3-*Q*-methyl-glucose	carbon dioxide methyl formate	*	*	carbon dioxide methyl formate methyl chloride	2·4	0·8
α-Methyl-glucoside	carbon dioxide methyl formate	*	*	carbon dioxide methyl formate methyl chloride	3·1	1·4
Pectic Acid	carbon dioxide acetaldehyde	59	68	carbon dioxide furan methyl formate	61·8	60–61
Pectin	carbon dioxide methyl chloride methyl formate	54·0	63·0	carbon dioxide furan methyl formate methyl chloride	57·0	55–56

* Determinations not possible on these compounds, which volatilise before extensive decomposition begins.

shown in Table II, *e.g.*, for 1 hr reaction at 255°, arabinose gave 9·4% and rhamnose gave 10% apparent uronic acid content.

3. *Methylated sugars and polysaccharides*

Although 2,3,4,6-tetramethyl-D-glucopyranose is more stable than D-glucose in acid solution,[25] methylated sugars yield acidic decomposition products on acid decarboxylations.[1] Table IV shows some typical results for 150-min acid decarboxylation,[3] infrared experiments showing that >50% of the apparent acidity is through volatile products other than carbon dioxide.

As a result of the effects already discussed, gravimetric determinations of methylated polysaccharides give high results.

4. *Minimum temperature required for effective thermal decarboxylation*

Our results have indicated that thermal decomposition is markedly temperature-sensitive in the range 245°–265°, with a distinct change in the decomposition mechanism above 280°. Carbohydrate materials begin to decompose[17] at about 130°, and the suggestion[19] that decarboxylation of uronic acid groups occurs at 145–155° made us investigate if any analytically useful, more specific, decarboxylation reaction would be given at lower decomposition temperatures.

For *Acacia seyal* gum, heating for 2.5-hr periods at each of 165°, 180° and 200° gave apparent uronic contents of 0·7%, 1·0% and 2·8%, respectively. For alginic acid evolution of carbon dioxide became detectable at 140° and estimable on heating for 2 hr at 145°; the results of various experiments are shown in Table V.

These experiments were sufficient to show that (*a*) the extent of decomposition depends on the uronic material studied, and (*b*) the time required for complete thermal decarboxylation would be much greater than the 150-min required for acid decarboxylation. The investigations were therefore discontinued, although it appears that the very small endothermic reaction observed by Chesters and Thomson[19] at 145–155° cannot result directly from "decarboxylation",

TABLE V. THERMAL DECOMPOSITION OF ALGINIC ACID

Decomposition temp., °C	Period of heating, *hr*	Apparent uronic acid, %
165	2·5	11·2
165	16	41·6
180	2·5	40·0
200	2·5	51·0

CONCLUSIONS

Decomposition at 255° for 20 min gave quantitative results for galacturonic and alginic acids if a *gravimetric* finish was used. The results are distinctly time-dependent (see Fig. 2) and considerable over-decarboxylation can occur. Furthermore, the rate of evolution of carbon dioxide varies for different compounds; the required yield of carbon dioxide is only given after 40 min for glucurone and after 60 min for *Acacia seyal* gum. In no case was a quantitative yield obtained in 15 min at 255°, as was reported by Perlin.[20] The reason for this is difficult to understand. The time taken for samples to attain the oven temperature was very similar to that reported by Perlin: the temperatures reported here were actual *sample* temperatures, not nominal oven or retort temperatures; the zero-time used for the kinetic measurements was corrected to allow for the internal volume of the oven, which had no "dead-space".

In investigations of this kind, the reaction kinetics and the results may be dependent on the apparatus design, on the surface area of the sample, and on its rate of increase in temperature; in agreement with Perlin,[20] all that can be done is to ensure, by careful apparatus design, that all the reaction conditions and variables are closely reproducible from run to run for different compounds.

The amounts of carbon monoxide detected agreed with those reported.[20] The nitrogen flow-gas used in most of our experiments contained approx. 20 ppm of

oxygen; when this was removed the results, as reported,[20] were not significantly altered.

It is of fundamental importance that when only the acidity from carbon dioxide is measured, thermal decarboxylation is not complete in 2 hr at 255°. The considerable differences between the gravimetric and titrimetric results are a consequence of the volatile reaction products which accompany the carbon dioxide; these products affect the gravimetric determination to a large extent. It is of interest that the volatilisable reaction products react slowly in cold concentrated sulphuric acid, liberating acidic vapours which give an additional source of error.

These facts must be considered together with the marked temperature- and time-dependence of the reaction, the differing reaction-times required for different compounds, and the relatively larger errors caused by side-reactions and the decomposition of non-uronic materials. Thermal decarboxylation, in our experience, does not compare favourably with acidic decarboxylation as a reliable reaction of general applicability for the analysis of materials containing uronic acid groups.

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Zusammenfassung—Die von Perlin vorgeschlagene Methode zur Bestimmung von Uronsäure durch thermische Decarboxylierung wurde untersucht. Ein speziell konstruierter Ofen, mit besonders hoher Temperaturkonstanz, gestattete die thermische Zersetzung verschiedener Verbindungen mit guter Reproduzierbarkeit kinetisch zu studieren. Verhältnismässig grosse Fehler können bei der Bestimmung der entwickelten Kohlensäure auftreten. Resultate werden mitgeteilt und es wird geschlossen, dass die thermische Decarboxylierung mit der 150-Minuten-Säuredecarboxylierung als allgemeine analytische Methode nicht konkurrieren kann.

Résumé—Les auteurs ont étudié la méthode de décarboxylation thermique des acides uroniques, proposée par Perlin. Un four conçu spécialement, ayant une bonne stabilité de température, permettait d'étudier cinétiquement la décomposition thermique de différents composés, avec une bonne reproductibilité. Des erreurs comparativement grandes peuvent se produire dans le dosage de l'anhydride carbonique dégagé; ces erreurs dépendent de la nature des autres produites de réaction volatils. Des résultats caractéristiques sont donnés et les auteurs concluent que la décarboxylation thermique ne peut être comparée favorablement à la décarboxylation acide pendant 150 minutes comme méthode analytique générale.

REFERENCES

[1] D. M. W. Anderson, *Talanta*, 1958, **1**, 283.
[2] *Idem, ibid.*, 1959, **2**, 73.
[3] D. M. W. Anderson and S. Garbutt, *ibid.*, 1961, **8**, 605.
[4] K. U. Lefevre and B. Tollens, *Ber.*, 1907, **40**, 4513.
[5] S. Garbutt, Ph.D. Thesis, Edinburgh University, 1960.
[6] D. M. W. Anderson, *Analyst*, 1959, **84**, 50.
[7] C. R. Marshall and F. W. Norris, *Biochem. J.*, 1937, **31**, 1296.
[8] P. K. Saha, A. K. Mazumdar and P. B. Sarkar, *Textile Res. J.*, 1957, **27**, 85.
[9] C. T. Greenwood, J. H. Knox and E. Milne, *Chem. and Ind.*, 1961, 1878.
[10] H. G. Lento, J. C. Underwood and C. O. Willits, *Food Research*, 1960, **25**, 750.
[11] J. E. Hodge and E. C. Nelson, *Cereal Chem.*, 1961, **38**, 207.
[12] J. R. Katz, *Rec. Trav. Chim.*, 1934, **53**, 554.
[13] A. Thompson and M. L. Wolfrom, *J. Amer. Chem. Soc.*, 1958, **80**, 6618.

[14] I. E. Puddington, *Canad. J. Res.*, 1948, **26** B, 415.
[15] T. J. Schoch and C. C. Jensen, *Analyt. Chem.*, 1940, **12**, 531.
[16] Y. Nayudamma, K. T. Joseph and S. M. Bose, *J. Amer. Leather Chem. Assoc.*, 1961, **56**, 548.
[17] D. M. W. Anderson and N. J. King, *Talanta*, 1961, **8**, 497.
[18] H. Morita, *Analyt. Chem.*, 1956, **28**, 64.
[19] G. Chesters and S. C. Thompson, *Science*, 1961, **133**, 275.
[20] A. S. Perlin, *Canad. J. Chem.*, 1952, **30**, 278.
[21] D. M. W. Anderson, A. M. Bews, S. Garbutt and N. J. King, *J. Chem. Soc.*, 1961, 5230.
[22] F. Feigl, *Spot-tests in Organic Analysis*. Elsevier Publishing Co., Amsterdam, 1960.
[23] D. M. W. Anderson and J. L. Duncan, *Talanta*, 1961, **8**, 1.
[24] D. M. W. Anderson and M. A. Herbich, in press.
[25] W. N. Haworth, E. L. Hirst and V. S. Nicholson, *J. Chem. Soc.*, 1927, 1513.

Talanta, 1962, Vol. 9, pp. 699 to 714. Pergamon Press Ltd. Printed in Northern Ireland

PRECIPITATION OF NICKEL DIMETHYLGLYOXIMATE FROM HOMOGENEOUS SOLUTION

STUDIES OF THE REACTIONS OF BIACETYL, HYDROXYLAMINE AND NICKEL^{II}

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Summary—The reaction between biacetyl and hydroxylamine to form dimethylglyoxime was found to follow simple kinetics in the absence of nickel. However, with nickel^{II} present, the kinetic studies showed definite evidence for complex formation between biacetyl monoxime and nickel. This complex and others formed with nickel in the reaction mixture determines the overall rate of formation of nickel dimethylglyoximate. Supersaturation concentrations of several hundred times the equilibrium solubility of nickel dimethylglyoximate were attained in nucleation experiments. The kinetic and nucleation studies provide explanations for some previously anomalous experimental observations, *e.g.*, the persistent supersaturation in this system provides an explanation for the inability to precipitate completely small amounts of nickel^{II} with dimethylglyoxime. The yellow colour observed in the initial stage of the precipitation of nickel from homogeneous solution arises from dissolved nickel dimethylglyoximate.

IN a previous investigation, the precipitation of nickel dimethylglyoximate from homogeneous solution was used[1] as the basis of a gravimetric analytical method for nickel^{II}. In the reaction, in which dimethylglyoxime is generated in ammoniacal nickel solution, a yellow colour is formed in the solution before the precipitation of the nickel chelate. The yellow colour could be made to persist for over an hour before the appearance of the solid phase. In addition, it was also found that the presence of nickel^{II} had a catalytic effect upon the reaction between biacetyl and hydroxylamine, *i.e.*, dimethylglyoxime was produced in the early stages of the reaction faster than when nickel^{II} was absent from the solution.

Investigations were therefore undertaken to provide information about the reactions taking place in solution before and during the precipitation of nickel dimethylglyoximate.

REAGENTS AND APPARATUS

The nickel and biacetyl stock solutions used in these investigations were prepared as described previously.[1] The dimethylglyoxime (Distillation Products Co., Rochester, N.Y.) was used in very dilute aqueous solutions without further purification.

The biacetyl monoxime (Distillation Products Co.) contained some dimethylglyoxime which could not effectively be removed by successive recrystallisations from aqueous solution. It therefore became necessary to prepare a biacetyl monoxime solution free of dimethylglyoxime.

Preparation of biacetyl monoxime solution

A small amount of the impure biacetyl monoxime was dissolved in 200 ml of distilled water. Five g of ammonium chloride and 10 ml of nickel^{II} stock solution were added to the biacetyl monoxime solution. The pH was then adjusted to approximately 7·5 with ammonium hydroxide, and the solution was allowed to stand for several hours before the precipitate was removed by filtration. The filtrate was then acidified with hydrochloric acid and extracted with three successive 25-ml portions of diethyl ether to separate the biacetyl monoxime from nickel^{II} and the other inorganic material. The combined ether extracts were extracted with three successive 25-ml portions of 1*N* sodium hydroxide

solution in order to transfer the biacetyl monoxime (as the anion) back into aqueous solution. The combined alkaline extracts were neutralised with 6*N* hydrochloric acid. The addition of an ammoniacal nickel solution to a test portion of the resulting biacetyl monoxime solution did not produce the characteristic red precipitate of nickel dimethylglyoximate.

Purification of hydroxylamine hydrochloride

The reagent grade hydroxylamine hydrochloride (J. T. Baker Chemical Co., Phillipsburgh, N.J.) used in the kinetic and nucleation experiments was purified by recrystallisation from ethyl alcohol solution containing a small amount of water; the product was then dried over sodium hydroxide and anhydrous calcium chloride in a desiccator.

All other chemicals used in this study were reagent grade.

Apparatus

All pH measurements were made with a Beckman Model 9600 pH meter calibrated with a Beckman pH 7 buffer solution (No. 3581).

The polarographic studies were made with a Sargent Model XXI polarograph. The electrolysis vessel was thermostatted at 30·0 ± 0·2°.

The spectrophotometric studies were made with a Cary Model II spectrophotometer equipped with a thermostatted cell compartment.

PROPERTIES OF THE YELLOW SPECIES

In the absence of nickel, the reaction between biacetyl and hydroxylamine did not result in the formation of the yellow colour. Because the colour was only observed when nickel was present, it was apparent that it was caused by complex formation between nickel and one of the components in the reaction mixture. When a very dilute aqueous solution of dimethylglyoxime was added to a very dilute aqueous ammoniacal nickel solution, a yellow colour was observed before precipitation. The absorption spectra, from 4000 to 2200 Å, of this yellow solution and that obtained from a PFHS (precipitation from homogeneous solution) experiment were identical. This indicated that complex formation between nickel and dimethylglyoxime was responsible for the yellow colour.

When the component in the coloured aqueous solution was extracted by chloroform, the organic phase showed a spectrum identical to that of nickel dimethylglyoximate dissolved in chloroform. The extinction coefficients for the component in chloroform and in water were determined from colorimetric analysis of the nickel content of the yellow solutions with 2,3-quinoxalinedithiol.[2] On the assumption that 1 atom of nickel is present in each molecule, the extinction coefficient ($1{\cdot}70 \times 10^3$) for the component extracted into the chloroform phase matched very well the extinction coefficient for nickel dimethylglyoximate in chloroform ($1{\cdot}72 \times 10^3$). It was found that when aqueous ammoniacal solutions containing nickel dimethylglyoximate crystals were heated nearly to boiling, yellow-coloured solutions were produced which exhibited spectra again identical to that obtained for the previously described yellow aqueous solution.

If nickel dimethylglyoximate were to dissociate into a 1:1 complex and free dimethylglyoxime, as indicated in the following equation:

$$NiD_2 \rightarrow NiD + D$$

where

NiD_2 = nickel-dimethylglyoximate

NiD = nickel-dimethylglyoxime 1:1 complex

D = dimethylglyoxime

the presence of free dimethylglyoxime should be spectrophotometrically observable in

such solutions. Because dimethylglyoxime was not so detected, 2 molecules of dimethylglyoxime must be associated with each atom of nickel in the complex. Diehl[3] discusses yellow or green-yellow compounds which are 1:1 complexes of nickel and the amphiform of dioximes; obviously, these compounds and the yellow species previously described are not identical.

When aqueous solutions containing the yellow species were "seeded" with nickel dimethylglyoximate crystals, the yellow colour slowly disappeared. Similarly, when aqueous solutions containing the yellow species were shaken vigorously, a red precipitate of nickel dimethylglyoximate was obtained. All of the experimental observations point to the conclusion that it is dissolved nickel dimethylglyoximate which is responsible for the yellow coloured aqueous solutions.

The difference in colour between the yellow solution species (aqueous or organic) and the red crystalline solid may result from the state of aggregation of nickel dimethylglyoximate. In the crystalline solid, the nickel dimethylglyoximate molecules are separated by an interplanar spacing[4] of 3·245 Å. Under these conditions there is the possibility that a particular excited electronic state in the monomer would interact in the crystalline aggregate so as to produce a red shift.[5]

KINETIC STUDIES

PRELIMINARY INVESTIGATIONS

In order to find a method for studying the reactions between biacetyl, hydroxylamine, and nickel^{II} in aqueous ammoniacal solution, attempts were made to follow changes in the concentrations of the various components in the reaction solution by spectrophotometric and polarographic techniques. As a first step, aqueous solutions of biacetyl, hydroxylamine, biacetyl monoxime, dimethylglyoxime, nickel dimethylglyoximate, nickel-ammonia complex, and nickel-hydroxylamine complex were each studied individually, in order to determine both their visible and ultraviolet absorption spectra, and their polarographic half-wave potentials. The absorption spectra of aqueous solutions of biacetyl monoxime, dimethylglyoxime, and nickel dimethylglyoximate are shown in Fig. 1.

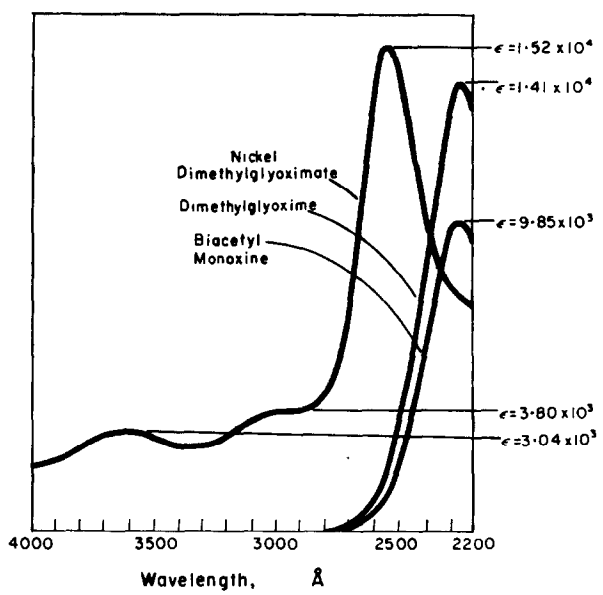


FIG. 1.—The absorption spectra of aqueous solutions of biacetyl monoxime, dimethylglyoxime, and nickel dimethylglyoximate.

It became apparent that it would be extremely difficult to follow the changes in concentration of the various components in the reaction solution by polarographic methods because there was not sufficient separation in the polarographic half-wave potentials. It was also found that it would be difficult to follow the changes in concentration of any component, except that of nickel dimethylglyoximate, by spectrophotometric means because of overlapping spectra, *e.g.*, the absorption maxima for dimethylglyoxime and biacetyl monoxime both occur at 2250 Å.

Because of the difficulties of utilising the spectrophotometric method for a complete kinetic study, a separation technique was then developed capable of determining the individual concentrations of biacetyl monoxime, dimethylglyoxime, and nickel dimethylglyoximate.

SEPARATIONAL PROCEDURE

(*a*) *Experimental*

The separation technique was based upon three factors.

First, the nickel dimethylglyoximate precipitate can be filtered from the reaction solution at any time, and subsequently determined colorimetrically.

Secondly, the biacetyl monoxime and dimethylglyoxime can be separated from hydroxylamine by ether extraction. Hydroxylamine is much more soluble in water than it is in ether and, therefore, this operation effectively stops the reaction at the time of the extraction.

Thirdly, because biacetyl monoxime and dimethylglyoxime are acidic, they can be transferred back into aqueous solution by extraction with 1*N* sodium hydroxide, and individually determined polarographically by adjustment of the pH of the alkaline solution to a value which gives a sufficient separation in the polarographic half-wave potentials.

Details of separation

A schematic diagram of the separations involved is shown in Fig. 2; the detailed procedure is as follows:

The hydroxylamine hydrochloride to be used in the kinetic experiment was weighed to the nearest 0·1 mg, transferred to a 150-ml beaker and dissolved in about 50 ml of distilled water; an appropriate aliquot of nickel^{II} stock solution was added to it. The solution was diluted to about 100 ml with distilled water, and the pH was adjusted to a desired value with ammonium hydroxide solution.

The solution was quantitatively transferred to a 250-ml volumetric flask and diluted to about 230 ml with distilled water. The volumetric flask was then placed, along with another flask containing biacetyl stock solution, in a constant temperature bath to reach temperature equilibrium.

The experiment was initiated when an aliquot of the biacetyl stock solution was pipetted into the 250-ml volumetric flask and the reaction mixture was diluted to volume with distilled water. The solution in the flask was carefully mixed and the time was noted.

A sample of this reaction solution was placed in a thermostatically controlled spectrophotometric cell in the spectrophotometer, and the supersaturation concentration of nickel dimethylglyoximate was determined spectrophotometrically at 3600 Å.

Ten-ml aliquots of the reaction mixture were also pipetted into test tubes which were then placed in the constant temperature bath. When the concentrations of biacetyl monoxime, dimethylglyoxime, and the amount of nickel dimethylglyoximate precipitated were to be determined, a 10-ml aliquot was quantitatively transferred to a 15-ml medium glass frit crucible.

The solution was quickly filtered through the crucible into a 60-ml separatory funnel, the precipitate was washed with a small amount of distilled water, and the amount of nickel dimethylglyoximate was determined colorimetrically according to the method of Passamaneck.[6]

One ml of 6*N* hydrochloric acid was added to the filtrate contained in the separatory funnel. The biacetyl monoxime and dimethylglyoxime were extracted first with one 20-ml portion of diethyl ether and then with two successive 10-ml portions of the ether. The combined ether extracts were extracted with three successive 20-ml portions of 1*N* sodium hydroxide solution. The combined alkaline extracts were then acidified with 6*N* hydrochloric acid to pH 2·5 $\pm$ 0·2 just before polarographic analysis. The solution was quantitatively transferred to a 100-ml volumetric flask, diluted to 100 ml with distilled water, and then subjected to polarographic analysis for the biacetyl monoxime and dimethylglyoxime.

(*b*) *Results and discussion*

The aqueous phase reaction of biacetyl with hydroxylamine at various pH values and in the absence of nickel^{II} was also studied by use of the separational procedure.

These reactions are indicated below:

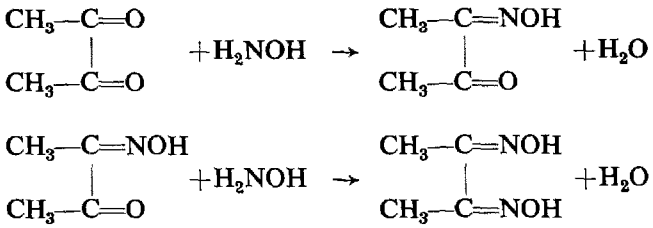
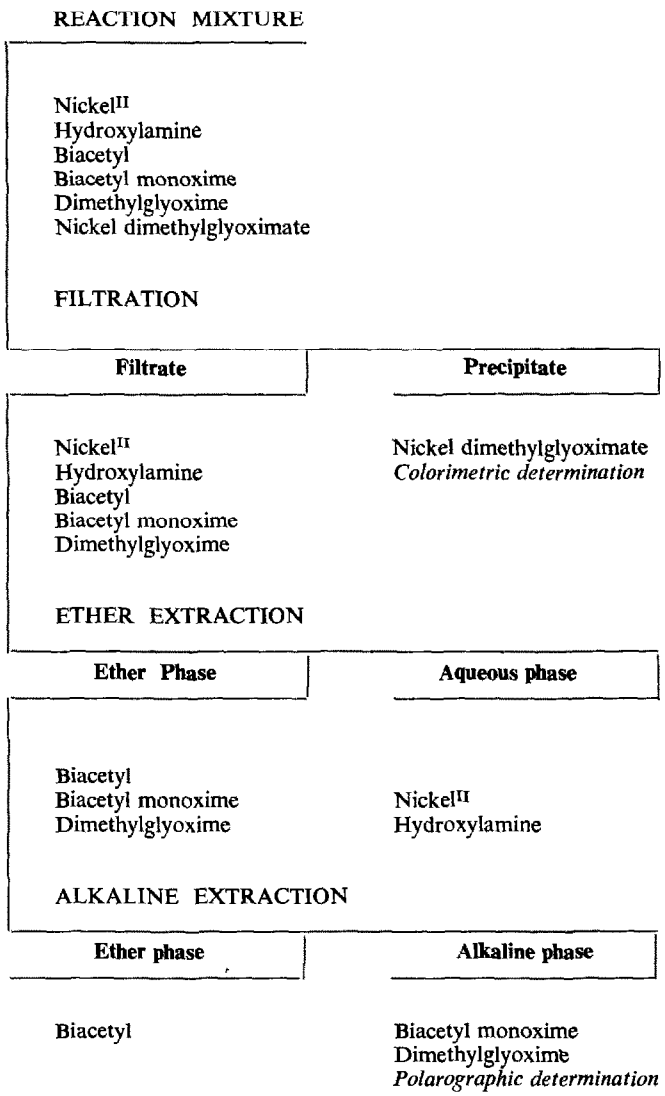


FIG. 2.—Schematic diagram of separations involved in the separational procedure



The equations can be expressed in the following simplified manner:

$$B + H \xrightarrow{k_1} M \tag{1}$$

$$M + H \xrightarrow{k_2} D \tag{2}$$

where
B = solution concentration of biacetyl,
H = solution concentration of hydroxylamine,
M = solution concentration of biacetyl monoxime,
D = solution concentration of dimethylglyoxime,
k_1 = rate constant for reaction (1),
k_2 = rate constant for reaction (2).

If both reactions are first order with respect to each reactant, then

$$-\frac{dB}{dt} = k_1HB \tag{3}$$

$$\frac{dM}{dt} = k_1HB - k_2HM. \tag{4}$$

If the initial hydroxylamine concentration is much larger than the initial biacetyl concentration so that the hydroxylamine concentration can be considered to be constant throughout the course of the reaction, then:

$$-\frac{dB}{dt} = k_1'B \tag{5}$$

$$\frac{dM}{dt} = k_1'B - k_2'M \tag{6}$$

and

$$B = B_0e^{-k_1't} \tag{7}$$

$$M = \frac{k_1'B_0}{k_2' - k_1'}(e^{-k_1't} - e^{-k_2't}) \tag{8}$$

where

t = time,
$k_1' = k_1H$,
$k_2' = k_2H$,
B_0 = initial solution concentration of biacetyl.

If $k_1' > k_2'$, when t is large enough, $e^{-k_2't} \cong 0$ and,

$$M = -\frac{k_1'B_0}{k_2' - k_1'}e^{-k_2't} \tag{9}$$

$$\frac{M}{B_0} = -\frac{k_1'}{k_2' - k_1'}e^{-k_1't} \tag{10}$$

$$-\ln\frac{B_0}{M} = \ln\left(-\frac{k_1'}{k_2' - k_1'}\right) - k_2't \tag{11}$$

$$\ln\frac{B_0}{M} + \ln\left(-\frac{k_1'}{k_2' - k_1'}\right) = k_2't. \tag{12}$$

A plot of ln (B_0/M) versus t should give a straight line with a slope equal to k_2' with intercept $\cong$ 0.

Quantitative information about reaction (2) could be obtained. However, it was impossible to gain more than qualitative information about the relatively faster reaction (1) owing to the uncertainties necessarily introduced into the experiments because of the sampling technique, *i.e.*, the successive ether extractions require several minutes to complete, which makes it difficult to know exactly when the reactions were stopped. Also, the reaction solutions are acidified just before extraction. This is necessary to ensure that the oximes are present in the acidic form, so that they can be extracted into the ether phase, but errors are introduced because of the change in pH of the reaction solution.

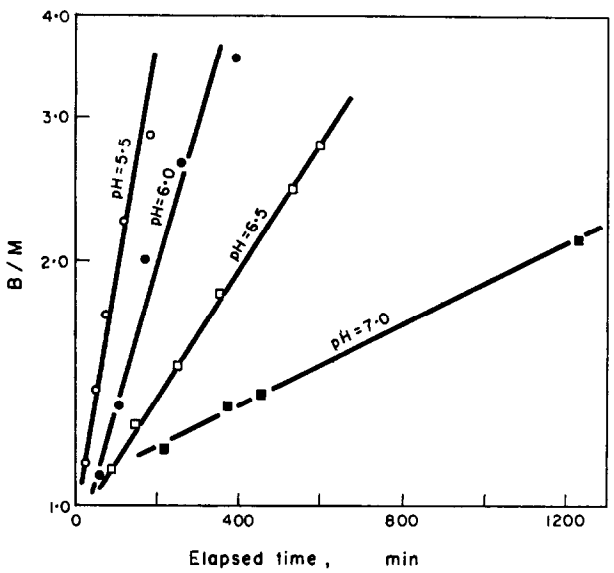
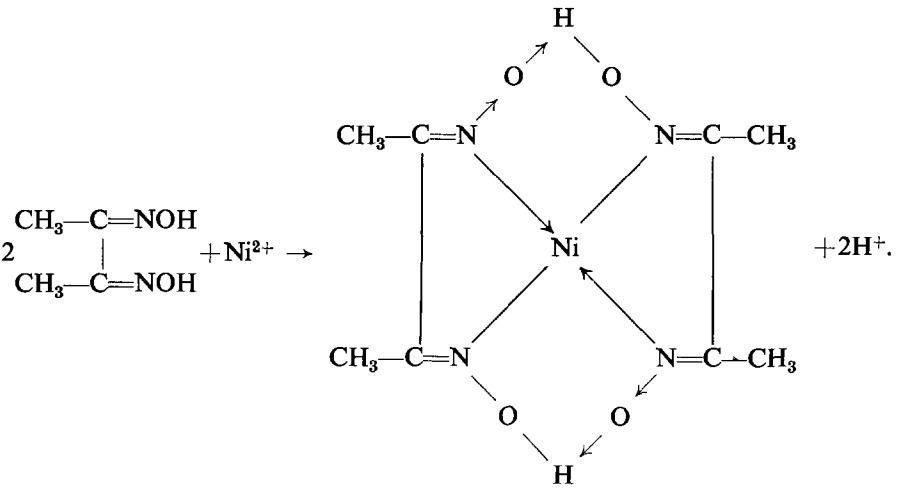


FIG. 3.—Ln (B_0/M) versus time for the reaction of biacetyl with hydroxylamine in the absence of nickel^{II} at various pH values
Initial biacetyl concentration: 9·2 × $10^{-4}M$
Initial hydroxylamine concentration: 1·0 × $10^{-1}M$
Temperature: 15·0°

Because the amount of hydroxylamine taken was much greater than that of biacetyl, the hydroxylamine concentration was effectively unchanged throughout the course of the reaction. Reaction (2) was found to be first order with respect to biacetyl monoxime, as is indicated by the straight lines obtained in a plot of ln (B_0/M) versus time. The rate of reaction was found to increase with increased solution acidity (from pH 6·0 to 5·5). These results are summarised in Fig. 3.

As indicated previously, the reaction of biacetyl with hydroxylamine in the presence of nickel^{II} was studied at various pH values through the use of the sampling technique. As before, the amount of hydroxylamine taken was much greater than that of biacetyl.

When nickel^{II} is present in the reaction solution, reactions (1) and (2) occur; however, the dimethylglyoxime formed reacts with nickel to produce the nickel dimethylglyoximate chelate:



Proceeding as before:

$$2D + N \xrightarrow{k_3} ND_2 \qquad (13)$$

where

D = Solution concentration of dimethylglyoxime

Ni = Solution concentration of nickel^{II}

NiD_2 = Nickel dimethylglyoximate concentration

k_3 = Rate constant for reaction (13)

A mass balance of the solution at any time yields:

$$B + M + D + 2NiD_2 = \text{constant} = B_0. \qquad (14)$$

If $k_3 \gg k_2$, the dimethylglyoxime reacts with nickel^{II} in reaction (13) faster than it is produced in reaction (2), and the concentration of free dimethylglyoxime in the reaction solution at any time is negligible, *i.e.*,

$$2ND_2 = B_0 - B - M. \qquad (15)$$

Thus, the concentration of nickel dimethylglyoximate can be expressed as a function of the biacetyl and the biacetyl monoxime concentration at any time. As assumed by equation (15), it was also found experimentally that free dimethylglyoxime could not be detected in the reaction solution as long as there was enough nickel^{II} to react with the dimethylglyoxime as it is being generated.

The reaction which produces dimethylglyoxime in the presence of nickel appears to be quite complex. It is not first order with respect to biacetyl monoxime as it is in the case when nickel is absent. The production of dimethylglyoxime in the early stages of the reaction is much faster when nickel is present in the reaction solution, but the rate of generation of dimethylglyoxime gradually decreases until, in the later stages of the reaction, the rate is much slower than when nickel is absent from the reaction solution.

SPECTROPHOTOMETRIC PROCEDURE

(*a*) *Experimental*

Because the preliminary kinetic studies utilising the separational procedure indicated that the concentration of dimethylglyoxime uncombined with nickel was negligibly small, the kinetic study was

simplified to a great extent, *i.e.*, the concentration of biacetyl monoxime in the reaction solution could be determined directly by spectrophotometric methods because of the lack of interference from dimethylglyoxime.

Procedure: Twice the amount of hydroxylamine hydrochloride to be used in the kinetic experiment was weighed to the nearest 0·1 mg and quantitatively transferred to a 100-ml beaker. Twice the required amount of nickel^{II} stock solution was pipetted into the beaker and the solution diluted to about 50 ml with distilled water. The pH was adjusted to the desired value with ammonium hydroxide, and the solution was quantitatively transferred to a 100-ml volumetric flask, and diluted to volume with distilled water. The solution was carefully mixed and then divided into two equal portions, which were transferred to 100-ml volumetric flasks. One solution was diluted to 100 ml with distilled water, carefully mixed, and set aside to be used as a spectrophotometric blank. The other solution was diluted to approximately 80 ml with distilled water and placed in the constant temperature bath.

A biacetyl solution was prepared by pipetting 0.200 ml of redistilled biacetyl into a 100-ml volumetric flask just before it was to be used experimentally. Water was added to dissolve the biacetyl and the solution diluted to volume. A 10-ml aliquot of this solution was pipetted into a second 100-ml volumetric flask. This solution was brought up to volume with distilled water, carefully mixed, and placed in the constant temperature bath. The biacetyl concentration of this solution was $2.16 \times 10^{-3} M$.

The solutions were allowed to remain in the constant temperature bath until they reached the desired temperature. The experiment was started when an aliquot of the biacetyl solution was pipetted into the flask containing the nickel and hydroxylamine, and the volume brought up to 100 ml with distilled water. The solution was carefully mixed, and a sample of it was placed in a thermostatically controlled spectrophotometric cell in the spectrophotometer. At intervals the supersaturation concentration of nickel dimethylglyoximate was determined at 3600 Å, the concentration of biacetyl monoxime at 2250 Å, and the component of each of these spectra produced by light scattering from the precipitate at 5600 Å.

(*b*) *Results and discussion*

If the absorbances of the biacetyl monoxime and dimethylglyoxime in the reaction solution are each quantitatively related to their respective concentrations, and if the solutions are sufficiently dilute, so that Beer's law holds, then:

$$M = \frac{A_M}{b\varepsilon_M} \tag{16}$$

$$D = \frac{A_D}{b\varepsilon_D} \tag{17}$$

and,

$$A = A_M + A_D \tag{18}$$

where M = solution concentration of biacetyl monoxime,
D = solution concentration of dimethylglyoxime,
b = length of spectrophotometric cell in cm,
ε_M = molecular extinction coefficient for biacetyl monoxime,
ε_D = molecular extinction coefficient for dimethylglyoxime,
A_M = absorbance due to biacetyl monoxime,
A_D = absorbance due to dimethylglyoxime,
A = total absorbance of the solution,

because the absorption maxima for both biacetyl monoxime and dimethylglyoxime occur at the same wavelength (2250 Å). Substitution of equations (16) and (17) into equation (18) yields:

$$A = b\varepsilon_M M + b\varepsilon_D D. \tag{19}$$

If the cell path length is always 1 cm

$$A = M\varepsilon_M + D\varepsilon_D. \tag{20}$$

A mass balance of the reaction solution yields

$$B + M + D = \text{constant} = B_0. \tag{21}$$

Substitution of equations (7) and (8) into equation (21) yields

$$D = B_0 - B_0 e^{-k_1' t} - \frac{k_1' B_0}{k_2' - k_1'} (e^{-k_1' t} - e^{-k_2' t}), \tag{22}$$

and substitution of equations (8) and (22) into equation (19) yields

$$A = B_0 \left[\frac{(\varepsilon_M - \varepsilon_D) k_1'}{k_2' - k_1'} (e^{-k_1' t} - e^{-k_2' t}) + \varepsilon_D (1 - e^{-k_1' t}) \right]. \tag{23}$$

If $k_1 \gg k_2$, $\frac{k_1'}{k_2' - k_1'} \cong -1$, and when t is large, $e^{-k_1' t} \cong 0$. Equation (23) then becomes

$$A = B_0 (\varepsilon_M - \varepsilon_D) e^{-k_2' t} + B_0 \varepsilon_D. \tag{24}$$

When t is small, $e^{-k_2' t} \cong 1$ and equation (23) becomes

$$A = B_0 [\varepsilon_D (1 - e^{-k_1' t}) - (\varepsilon_M - \varepsilon_D)(e^{-k_1' t} - 1)]. \tag{25}$$

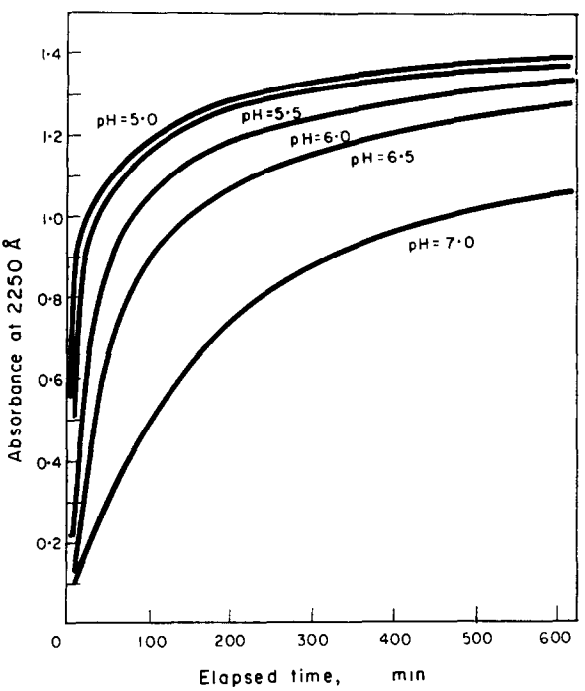


FIG. 4.—Absorbance versus time for the continuous spectrophotometric determination of biacetyl monoxime and dimethylglyoxime
Initial biacetyl concentration: $1{\cdot}08 \times 10^{-4} M$
Initial hydroxylamine concentration: $7{\cdot}20 \times 10^{-2} M$
Temperature: 15·0°

Equations (24) and (25) indicate that quantitative information about reactions (1) and (2) can be obtained through the use of spectrophotometric techniques, because the total absorbance of the reaction solution at 2250 Å is functionally related to the rate constants of both reactions.

Equations (24) and (25) were used to evaluate the spectrophotometric results (obtained directly from the recording spectrophotometer as absorbance versus time graphs, *cf.* Fig. 4). When t was large, $e^{-k_1't} \simeq 0$, and equation (24) was solved for k_2'. When t was small, $e^{-k_2't} \simeq 1$, and equation (25) was solved for k_1'. The two constants were then adjusted when necessary by trial and error methods so that equation (23) was true at all times. The result of the experiments are summarised in Figs. 5 and 6.

The experimental results obtained from the spectrophotometric kinetic study of the reactions between biacetyl and hydroxylamine in the presence of nickel^{II} are summarised in Figs. 7 and 8. These results substantiate the information obtained from the separational procedure. The same characteristic reactivity of biacetyl monoxime was

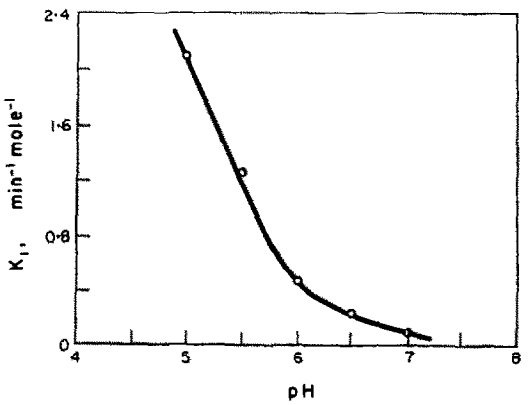


FIG. 5.—Rate constant, k_1, versus pH for the generation of biacetyl monoxime from biacetyl and hydroxylamine in the absence of nickel^{II}
Initial biacetyl concentration: $1{\cdot}08 \times 10^{-4}M$
Initial hydroxylamine concentration: $7{\cdot}20 \times 10^{-2}M$
Temperature: 15·0°

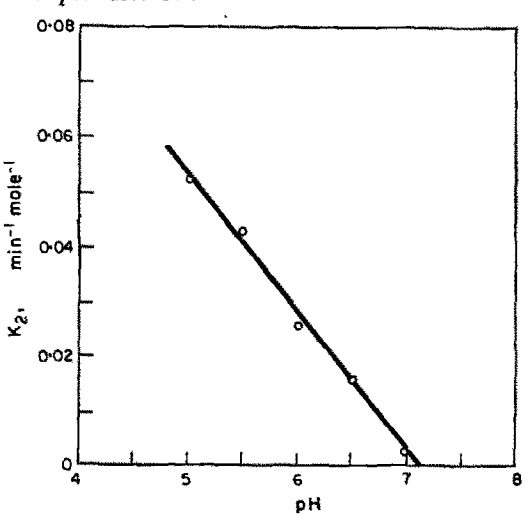


FIG. 6.—Rate constant, k_2, versus pH for the generation of dimethylglyoxime from biacetyl monoxime and hydroxylamine in the absence of nickel^{II}
Initial biacetyl concentration: $1{\cdot}08 \times 10^{-4}M$
Initial hydroxylamine concentration: $7{\cdot}20 \times 10^{-2}M$
Temperature: 15·0°

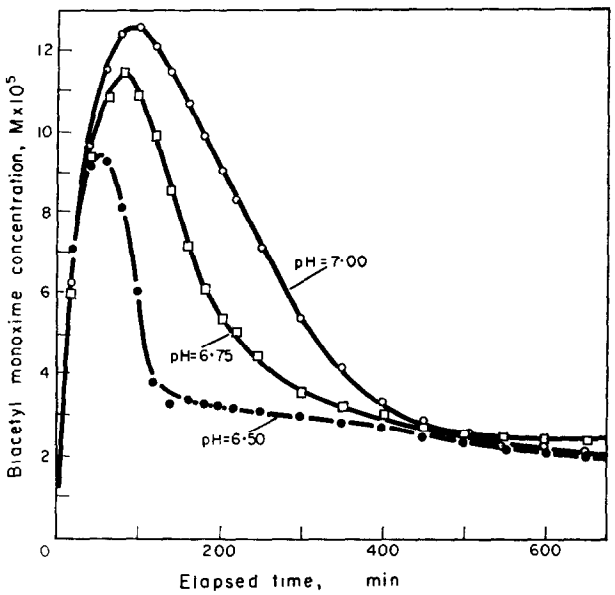


FIG. 7.—Biacetyl monoxime concentration versus time for the reaction between biacetyl and hydroxylamine in the presence of nickel^{II} (three typical experiments)
Initial biacetyl concentration: $2{\cdot}16 \times 10^{-4}M$
Initial hydroxylamine concentration: $7{\cdot}20 \times 10^{-2}M$
Initial nickel^{II} concentration: $3{\cdot}36 \times 10^{-3}M$
Temperature: 15·0°

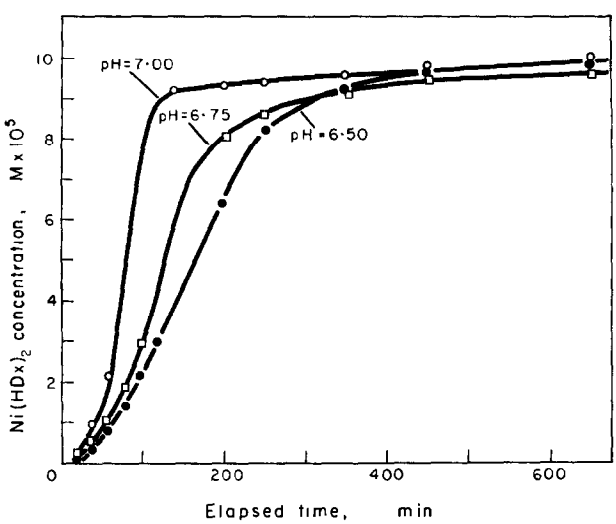
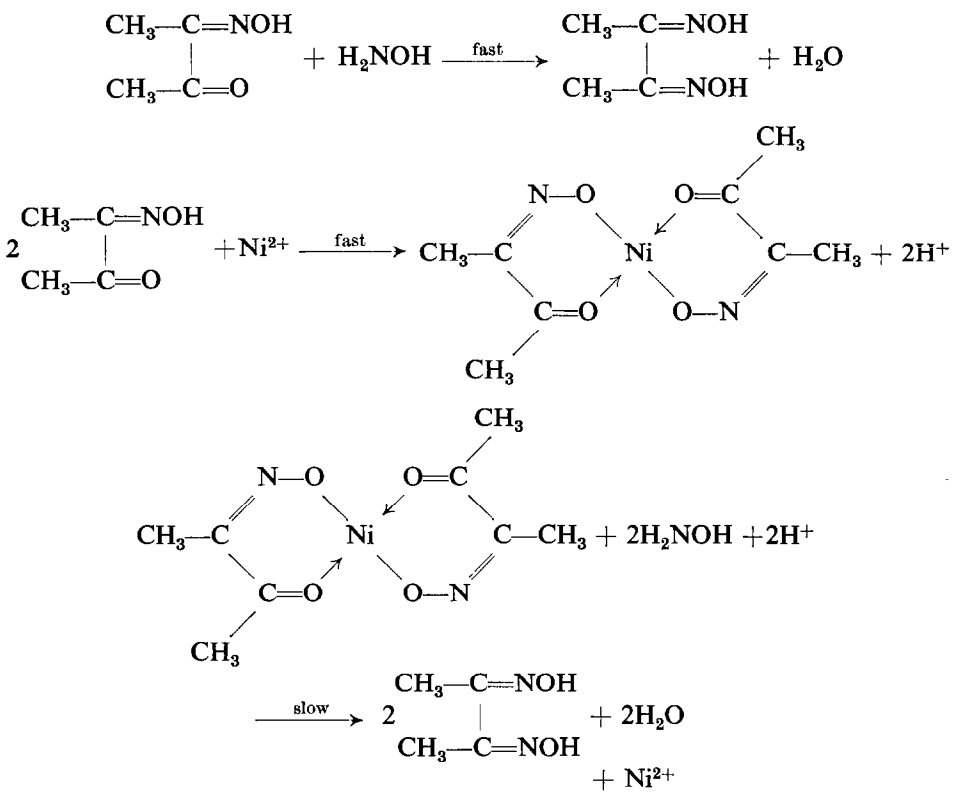


FIG. 8.—Total nickel dimethylglyoximate (precipitated and in solution) versus time for the reaction between biacetyl and hydroxylamine in the presence of nickel^{II} (three typical experiments)
Initial biacetyl concentration: $2{\cdot}16 \times 10^{-4}M$
Initial hydroxylamine concentration: $7{\cdot}20 \times 10^{-2}M$
Initial nickel^{II} concentration: $3{\cdot}36 \times 10^{-3}M$
Temperature: 15·0°

observed, *i.e.*, the reactivity of biacetyl monoxime in the early stages of the reaction is much greater when nickel is present, but the reactivity gradually decreases until, in the later stages of the reaction, the rate is slower than when nickel is absent from the reaction solution. As was observed in experiments utilising the separational procedure this effect became more pronounced with decreased solution acidity from pH 6·5 to 7·0.

The complicated reactivity of biacetyl monoxime under these circumstances can possibly be partially explained by the formation of a relatively stable intermediate complex between biacetyl monoxime and nickel^{II}. Evidence for such complex formation was obtained from experiments in which the individual spectra of separate ammoniacal solutions of biacetyl monoxime and nickel^{II} were compared with the spectrum of a mixture of biacetyl monoxime and nickel^{II} in ammoniacal solution. The spectrum of the mixture was not a simple combination of the spectra of the two individual components of the mixture. A definite absorption maximum was observed at 3020 Å which was not observed in either of the other individual spectra, and if the mixture is concentrated enough the solution appears brown coloured. This intermediate complex could be formed at a rate comparable to the rate of the reaction between uncomplexed biacetyl monoxime and hydroxylamine, so the total process might be as follows:



Because the first and second reactions could both occur, the total net result would be a more rapid decrease in the biacetyl monoxime concentration in the early stages of

the kinetic run than in the case when nickel^{II} is absent from the reaction solution. As the free biacetyl monoxime concentration is reduced to zero, the only remaining species capable of reaction with hydroxylamine is the relatively unreactive nickel complex. It is reasonable to assume that all of the biacetyl would, therefore, not be converted to nickel dimethylglyoximate under these conditions. This could account for the consistently low results obtained by Barnicoat[7] in his attempts to determine quantitatively biacetyl at room temperature.

Adding to the complexity of the reaction of biacetyl monoxime with hydroxylamine in the presence of nickel^{II} is the fact[8,9] that hydroxylamine also forms coordination compounds with nickel^{II}. The reactivity of each one of these compounds probably differs from those of the others and from the reactivity of free hydroxylamine.

These complexes and the complex between biacetyl monoxime and nickel^{II} become increasingly disassociated in increasingly acidic solutions. It should be expected, then, that as the reaction solution acidity is increased, the reactivity of biacetyl monoxime in nickel^{II} solution should approach the reactivity of biacetyl monoxime in nickel^{II} free solutions. This was experimentally observed (*cf.* Fig. 7).

NUCLEATION STUDIES

(*a*) *Experimental*

The generation and solution supersaturation of nickel dimethylglyoximate was followed spectrophotometrically during each experimental run. The absorbance-time curves were obtained with the

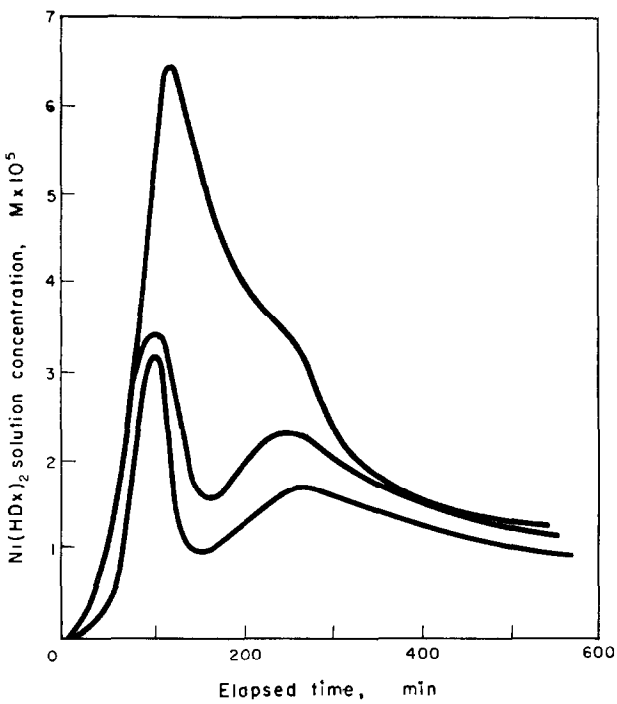


FIG. 9.—Degree of supersaturation versus time for the precipitation of nickel dimethylglyoximate from homogeneous solution (three typical experiments)
Equilibrium solubility of $Ni(HDx)_2$ in aqueous salt solution[6] $= 2 \times 10^{-7} M$

recording spectrophotometer. The component of the total absorbance caused by light scattering from the precipitate was determined at 5600 Å and subtracted from the absorbance observed at 3600 Å in order to obtain the true solution concentration of nickel dimethylglyoximate at any time.

(b) Results and discussion

Typical results of these experiments are given as the supersaturation-time curves of Fig. 9. The solution concentration of nickel dimethylglyoximate increased to a point well beyond the equilibrium solubility concentration, as determined by Christopherson and Sandell;[10] supersaturation concentrations of several hundred times the equilibrium solubility of nickel dimethylglyoximate were attained.

Another unusual phenomenon which occurred in certain experiments was an increase in the supersaturation (*cf.* Fig. 9) of the solution well after the initial decrease in the supersaturation was observed. This could be caused by settling of the precipitate particles which nucleate in the first "burst" so that subsequent growth on them does not occur at a rate which is rapid enough to relieve the solution of all of the nickel dimethylglyoximate which is being generated in the solution. The supersaturation of the solution would then increase again until another "burst" of precipitate particles occurs.

An attempt was made to apply the method of Klein, Gordon, and Walnut[11] to determine the precipitation nucleus of nickel dimethylglyoximate. No apparent correlation between the area under the supersaturation-time curve and the number of precipitate particles obtained from an arbitrary volume of reaction solution for this system was found. It is possible that the multiple precipitation "bursts" are responsible for this lack of correlation, and that not only the area under the curve but the shape of the curve is important in any determination of the nucleus size for the nickel dimethylglyoximate system.

The persistent supersaturation of the solutions containing nickel dimethylglyoximate serves to explain some previous anomalous experimental observations. One of these is the observation of Jones,[12] who found that amounts of nickel in steel as high as 0·1 % were frequently reported as "traces". When the amount of nickel was less than 0·06 %, some nickel was quite certainly not precipitated even on prolonged standing. To check these results, Jones took various amounts of nickel and carried out the precipitation, as usual in slightly ammoniacal solution, in a volume of 100 ml. After the solutions were allowed to stand overnight, the precipitate was filtered but was not washed, and the nickel in the filtrate was determined colorimetrically. The results of these experiments are given in Table I.

TABLE I

Weight of nickel taken, *g*	Nickel found in filtrate, %
0·0001	35·0
0·0002	7·5
0·0003	5·0
0·00075	2·0
0·0010	2·25
0·0015	1·0
0·0020	0·25
0·0025	negligible

Equilibrium solubility could not account for such large amounts of nickel in the filtrate.

Finally, Komarek[13] observed in freshly precipitated nickel dimethylglyoximate solutions a polarographic wave which disappeared after a few minutes. It is reasonable to suspect that this is the same wave observed in the previously described preliminary polarographic experiments, and which can be attributed to the supersaturation of nickel dimethylglyoximate.

Zusammenfassung—Die Reaktion zwischen Diacetyl und Hydroxylamin (Bildung von Dimethylglyoxim) nimmt in Abwesenheit von Nickel einen einfachen Verlauf. In Gegenwart von Nickel jedoch zeigen kinetische Studien, dass Komplexbildung zwischen Diacetyl, Monoxim und Nickel auftritt. Dieser Komplex und andere Komplexe, die in der Mischung auftreten, bestimmen die Geschwindigkeit der Bildung von Nickeldimethylglyoxim. Übersättigungskonzentrationen hundert und mehrmals grösser als die Gleichgewichtskonzentration für die Löslichkeit von Nickeldimethylglyoxim wurden während der Durchführung von Nukleationexperimenten erhalten. Das Studium der Raktionkinetik und Keimbildung erlaubt nun die Erklärung für verschiedene in früheren Experimenten beobachtete Abnormalitäten. Die starke Tendenz zu Übersättigung erklärt, warum kleine Nickelmengen nicht vollständig gefällt werden können. Die gelbe Färbung der Lösung, die man am Beginn der Nickelfällung aus homogener Lösung beobachtet, wird durch gelöstes Nickeldimethylglyoxim verursacht.

Résumé—Les auteurs ont trouvé que la réaction entre le biacétyle et l'hydroxylamine pour former la diméthyl-glyoxime suivait une cinétique simple en l'absence de nickel. Cependant, en présence de nickel(II), l'étude cinétique montre nettement la formation d'un complexe entre biacétyle, monoxime et nickel. Ce complexe et les autres formés avec le nickel dans le mélange réactionnel déterminent la vitesse globale de formation du diméthylglyoximate de nickel. Des concentrations de sursaturation de plusieurs centaines de fois la solubilité à l'équilibre du diméthylglyoximate de nickel sont atteintes dans les expériences d'amorçage. Les études de cinétique et d'amorçage fournissent les explications de quelques observations expérimentales considérées comme anormales, par exemple: la sursaturation persistante dans ce système explique l'inaptitude à précipiter complètement de faibles quantités de nickel(II) par la diméthylglyoxime. La couleur jaune observée au stade initial de précipitation du nickel en solution homogéne est due au diméthylglyoximate de nickel dissous.

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REFERENCES

[1] E. D. Salesin and L. Gordon, *Talanta*, 1960, **5**, 81.
[2] D. A. Skoog, Ming-Gon Lai and A. Furst, *Analyt. Chem.*, 1958, **30**, 365.
[3] H. Diehl, *The Application of the Dioximes to Analytical Chemistry*. The G. Frederick Smith Chemical Co., Columbus, Ohio, U.S.A., 1940.
[4] R. E. Rundle and L. E. Godycki, *Acta Cryst.*, 1953, **6**, 487.
[5] H. G. Drickamer and J. C. Zaher, *Analyt. Chem.*, 1960, **33**, 1625.
[6] E. Passamaneck, *Ind. Eng. Chem., Analyt.*, 1945, **17**, 256.
[7] C. R. Barnicoat, *Analyst*, 1935, **60**, 653.
[8] K. A. Jensen, *Z. anorg. Chem.*, 1944, **252**, 227.
[9] H. Yoneda, *Bull. Chem. Soc. Japan*, 1957, **30**, 132.
[10] H. Christopherson and E. B. Sandell, *Analyt. Chim. Acta*, 1954, **10**, 1.
[11] D. H. Klein, L. Gordon and T. H. Walnut, *Talanta*, 1959, **3**, 187.
[12] B. Jones, *Analyst*, 1929, **54**, 582.
[13] K. Komarek, *Coll. Czech. Chem. Comm.*, 1947, **12**, 399.

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A NEW REDUCTIMETRIC REAGENT: IRON^{II} IN A STRONG PHOSPHORIC ACID MEDIUM

TITRATION OF URANIUM^{VI} WITH IRON^{II} AT ROOM TEMPERATURE

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Summary—The formal redox potential of the Fe^{III}/Fe^{II} couple has been determined in media of varying phosphoric acid concentration, and found to decrease steeply with increasing phosphoric acid concentration. Above a certain concentration of phosphoric acid, the difference between the formal potentials of the U^{VI}/U^{IV} and Fe^{III}/Fe^{II} couples becomes sufficiently great to enable iron^{II} to reduce uranium^{VI} even at room temperature. This is the reversal of the normal redox reaction—oxidation of uranium^{IV} by iron^{III}. A careful study of the various factors involved has enabled us to develop a new reductimetric titration of uranium^{VI} with iron^{II} in strong phosphoric acid medium (11.0 to 13.5*M*) at room temperature using either a potentiometric end-point or a visual end-point with methylene blue or thionine as an internal redox indicator. Because the new procedure enables the titration to be carried out at room temperature, it is more convenient than procedures involving titanium^{III} and chromium^{II} which require temperatures ranging from 60 to 90°. The new procedure has a further advantage in that it can be used for the determination of uranium^{VI} even in the presence of iron^{III} and tungsten^{IV}, using an electrometric end-point. Also, the new procedure does not require the elaborate precautions which are necessary for the preparation and storage of titanium^{III} or chromium^{II} solutions.

IN 1955 Canning and Dixon[1] made the interesting observation that uranium^{VI} can be reduced to uranium^{IV} by heating to the boiling point with an excess of iron^{II} in a medium containing 40% (by volume) of orthophosphoric acid. They showed that the reaction can be employed for the spectrophotometric determination of uranium^{VI}. It is obvious that the reaction discovered by Canning and Dixon is the reversal of the normal redox reaction, in which uranium^{IV} is oxidised by iron^{III}. Because the new reaction appeared to offer interesting possibilities for the use of iron^{II} in a concentrated phosphoric acid medium as a powerful reductometric reagent, a systematic investigation of this reagent has been planned by Gopala Rao since 1955.

Linga Murty[14] determined the formal potentials of the Fe^{III}/Fe^{II} and U^{VI}/U^{IV} couples in media of varying phosphoric acid concentration. These determinations have afforded an explanation for the reversal of the normal redox reaction. The data presented in Tables I and II and the curves given in Fig. 1 show that the redox potential of the Fe^{III}/Fe^{II} couple decreases steeply on increasing the phosphoric acid concentration, while the redox potential of the U^{VI}/U^{IV} couple increases with increasing phosphoric acid concentration. It will be noted further that above a certain phosphoric acid concentration, the formal potential of the Fe^{III}/Fe^{II} couple attains a value lower than that of the U^{VI}/U^{IV} couple, the difference in the two potentials being sufficient to enable the reduction of uranium^{VI} by iron^{II}. The potential values

reported by Baes[2] and Marcus[3] are in general agreement with the values given here.

We have been able to establish conditions under which uranium^{VI} can be determined in concentrated phosphoric acid medium at room temperature by titration with a solution of iron^{II} sulphate, using either a potentiometric end-point or a visual end-point with methylene blue or thionine as an internal redox indicator. Although the actual reductant is a complex of iron^{II} and phosphoric acid, the complex need not be pre-formed and used as such. According to our procedure an iron^{II} sulphate solution is run from a burette into an uranium^{VI} solution containing 90% of syrupy phosphoric acid (volume by volume), the specific gravity of the syrupy phosphoric acid being 1·75 (89% by weight). Our method has the obvious advantage that the reagent is more stable than the usual reductometric reagents available for the titration of uranium^{VI}, namely titanium^{III} and chromium^{II}, which require special storage conditions. Furthermore, our reagent has the advantage that it enables the titrimetric determination of uranium^{VI} to be carried out at room temperature, whereas the titrations of uranium^{VI} with titanium^{III} or chromium^{II} have been recommended to be made at higher temperatures with consequential disadvantages.

Kolthoff and Tomicek[4] carried out the titration of uranium^{VI} with titanium^{III} chloride at 55–60°, employing a potentiometric end-point. Steur[5] considered this procedure unsatisfactory and improved it by the addition of tartrate to the uranyl salt solution. Minczewski, Przytycka and Kohman[6] carried out the titration of uranyl fluoride at 70° (in an atmosphere of carbon dioxide) with titanium^{III} chloride in the presence of Rochelle salt. Lingane and Iwamoto[7] prescribed the coulometric titration of uranium^{VI} to be carried out in a citrate medium (at pH 0·5 to 1·5) at 85° with titanium^{III}, electrogenerated by the reduction of titanium^{IV} at a mercury cathode. Flatt and Sommer[8] employed chromium^{II} for the titrimetric determination of uranium^{VI} in a hot acid medium (2·0 to 6·0*N* hydrochloric acid or 1·0 to 6·0*N* sulphuric acid). Investigating the same titration, Elshamy and Ed-Din Zayan[9] stated that the best titration of uranium^{VI} with chromium^{II} is possible in 8·0*N* hydrochloric acid at 90°. A further disadvantage of titanium^{III} and chromium^{II} is that they react with iron^{III}, with the result that they cannot be used for the titrimetric determination or uranium^{VI} in the presence of iron^{III}. The reagent now proposed by us is free from this defect.

EXPERIMENTAL

Determination of Formal Redox Potentials of Fe^{III}/Fe^{II} *and* U^{VI}/U^{IV} *Couples in a Concentrated Phosphoric Acid Medium*

Reagents

Uranium^{VI} solution: An approximately 0·025*M* solution in 1·0*N* sulphuric acid is prepared from Analytical Reagent Grade uranyl acetate supplied by Mallinkrodt Chemical Co., New York, U.S.A. The solution is standardised by reduction in a Jones reductor according to the customary procedure, followed by titration with a standard solution of cerium^{IV} sulphate according to the procedure prescribed by Gopala Rao and coworkers.[10]

Uranium^{IV} solution: A known volume of the uranium^{IV} solution is reduced electrolytically using a small platinum wire electrode as anode and a clean bright platinum gauze as cathode. The reduction is carried out for 10 hr at 4V. The resultant uranium^{IV} solution is standardised by the method already mentioned.

Iron^{II} solution: Prepared by dissolving a known weight of Analytical Reagent Grade iron wire in Analytical Grade sulphuric acid and diluting the resulting solution to a known volume. The solution is standardised by titration with a standard solution of sodium vanadate, using *N*-phenylanthranilic acid as indicator

Iron^{III} solution: Prepared by oxidising the iron^{II} solution with hydrogen peroxide.

Phosphoric acid: Syrupy phosphoric acid (89%, E. Merck) has been employed in these investigations.

Procedure

The free acid in the salt solutions prepared as described above has been determined according to the procedure of Schumb, Scherill and Sweetser.[11] Solutions of equimolar mixtures of iron^{III} and

TABLE I

Concentration of phosphoric acid, *moles per litre*	Formal redox potential (N.H.E.) of Fe^{III}/Fe^{II} couple, *V*	
	0·5*M* H_2SO_4	0·25*M* H_2SO_4
nil	0·684	0·680
0·177	0·626	0·594
0·355	0·594	0·566
0·532	0·577	0·552
0·886	0·558	0·532
1·770	0·521	0·500
2·660	0·503	0·481
3·550	0·491	0·472
5·320	0·468	0·440
7·090	0·448	0·429
7·980	0·438	0·425
8·920	0·429	0·415
9·810	0·420	0·409
10·690	0·411	0·400
11·58	0·400	0·388

iron^{II} are prepared by mixing solutions of these two salts in appropriate amounts to give a 0·01*N* solution with respect to total iron when diluted to 100 ml, sufficient sulphuric acid and phosphoric acid being added to give the desired concentrations. The solutions are allowed to attain the temperature of the thermostat (28° ± 0·1°) before measuring the potentials. It is observed that a bright platinum electrode (freshly heated) placed in the above solution readily acquires a stable potential. All the

TABLE II

Concentration of phosphoric acid, *moles per litre.*	Formal redox potential (N.H.E) of U^{VI}/U^{IV} couple, *V*	
	0.5*M* H_2SO_4	0.25*M* H_2SO_4
0.000	0.549	0·494
0·177	0·559	0·518
0·355	0·560	0·519
0·532	0·561	0·521
0·709	0·558	0·520
0·886	0·558	0·519
1·770	0·557	0·522
2·660	0·561	0·545
3·550	0·569	0·565
5·320	0·595	0·583
7·080	0·595	0·584
8·920	0·596	0·585
10·690	0·600	0·585

potentials have been measured using a saturated calomel electrode as a reference electrode and a saturated potassium chloride agar as the salt bridge. During the measurements, the iron salt solution is maintained under an atmosphere of nitrogen free from oxygen. The results are summarised in Table I.

From the results in Table I, it is evident that the formal redox potential of the Fe^{III}/Fe^{II} couple decreases with increasing concentration of phosphoric acid.

The formal redox potential of the U^{VI}/U^{IV} couple has also been measured in a phosphoric acid medium at a total uranium concentration of 0·01*M* and a temperature of 28° ± 0·1°. Considerable difficulty has been experienced in the attainment of steady potentials for this system. However, fairly reproducible values have been observed after waiting for 7–8 min, when the precaution is taken to ignite the bright platinum electrode several times. The results are summarised in Table II.

From the results in Table II, it is seen that the redox potential of the U^{VI}/U^{IV} couple slowly increases with increasing phosphoric acid concentration, even when the solution contains 0·25–0·5*M* sulphuric acid.

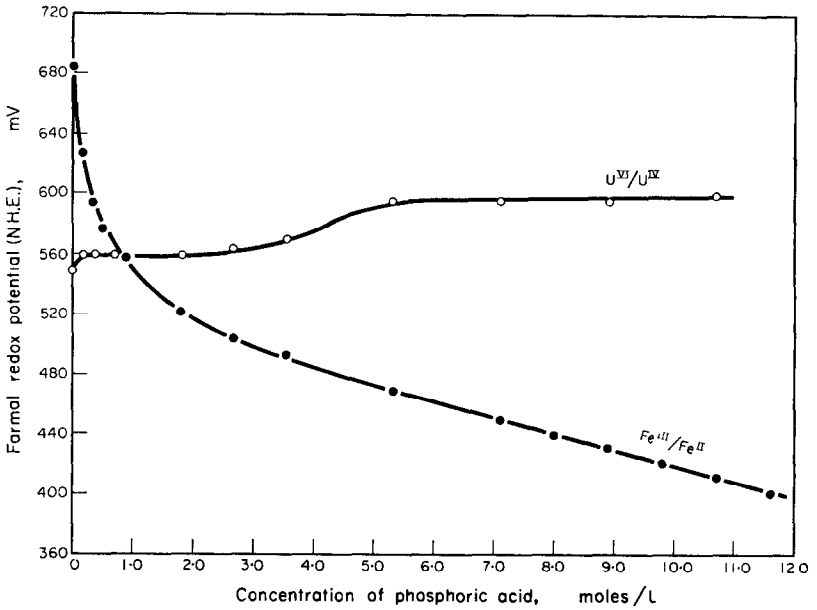


FIG. 1—Formal redox potentials of U^{VI}/U^{IV} and Fe^{III}/Fe^{II} couples in a phosphoric acid medium.

Fig. 1 gives the curves showing the variation of the formal redox potential with change in phosphoric acid concentration in each case. Besides phosphoric acid the mixture contains sulphuric acid at 0·5*M* concentration. It will be noted from the curves that the formal redox potential of the Fe^{III}/Fe^{II} couple has a value lower than that of the U^{VI}/U^{IV} couple when the concentration of phosphoric acid is 0·886*M* or higher. The difference between the formal potentials of the two systems is about 0·18 V at a concentration of phosphoric acid of 9·8*M* and this difference increases as the phosphoric acid concentration is increased further. There is thus a possibility that $iron^{II}$ may reduce $uranium^{VI}$ even in the cold when the phosphoric acid concentration is greater than 9·8*M*.

Photometric investigation of the reduction of uranium^{VI} by iron^{II} at varying phosphoric acid concentration

In order to ascertain the concentration of phosphoric acid at which a speedy reduction of $uranium^{VI}$ occurs, we have carried out a photometric study of a mixture of $uranium^{VI}$ with a slight excess of $iron^{II}$ at varying concentrations of phosphoric acid; the optical density of the mixture is noted at a wavelength of 660 mμ at varying times in a Klett-Summerson photoelectric colorimeter using optically matched tubes. Preliminary work has shown that this is the region at which $uranium^{IV}$ has a high absorption, while $iron^{III}$, $iron^{II}$ and $uranium^{VI}$ have negligible absorption in phosphoric acid solution. The results are presented in Table III.

The limiting value of the optical density for each system is obtained from a carefully prepared artificial mixture of $uranium^{IV}$, $iron^{II}$ and $iron^{III}$ sulphates and phosphoric acid at the corresponding concentrations. It is interesting to note that there is a slight change in the optical density of the $uranium^{IV}$ solution with changing phosphoric acid concentration, as revealed by the slight changes in the limiting values given in Table III. Similar observations have been made by Andrews, Schaap and Gates.[12] From the observations recorded in Table III, it is evident that the speed of reduction of $uranium^{VI}$ by $iron^{II}$ increases with increasing concentration of phosphoric acid. Under the conditions

of the experiments, the reaction is complete in less than 30 sec in media containing phosphoric acid at an overall concentration of 11·6*M* and above. Hence, we carried out electrometric titration of uranium^{VI} with iron^{II} at room temperature at two concentrations of phosphoric acid, *viz.* 11·6*M* and 13·1*M*.

Electrometric titration of uranium^{VI} with iron^{II} in concentrated phosphoric acid medium

Reagents

0·025*M uranyl acetate solution:* Prepared in 0·5*M* sulphuric acid and standardised according to the procedure already described.

TABLE III

Time, *min*	Photometer dial reading, Phosphoric acid concentration, *M*					
	5·7	7·3	8·7	10·2	11·6	13·1
0·5	—	—	—	34	36·5	37·0
2	5·0	15·0	29·0	34·5	36·5	37·0
10	13·0	27·0	34·0	34·5	36·5	37·0
15	17·0	30·5	34·0	34·5	36·5	37·0
30	24·5	33·0	34·0	34·5	36·5	37·0
60	28·0	33·5	34·0	34·5	36·5	37·0
120	30·0	33·5	34·0	34·5	36·5	37·0
300	33·0	33·5	—	—	—	—
600	33·0	33·5	—	—	—	—
Limiting value	33·0	33·5	34·0	34·5	36·5	37·0

5·0 ml of uranium^{VI} (0·02738*m*) + 1·2 ml of iron^{II} (0·5130*m*) + X ml of syrupy phosphoric acid + water to make up to 50 ml.

0·25*M iron^{II} solution:* Prepared from Mohr's salt in 0·5*M* sulphuric acid and standardised according to the procedure already described. The concentration of iron^{II} is kept high to keep the titre low so that the concentration of phosphoric acid in the mixture does not fall appreciably.

Syrupy phosphoric acid: For the bulk of the electrometric titrations syrupy phosphoric acid of B.P. grade supplied by Albright and Wilson Ltd., Birmingham, England, has been used. Control experiments with Merck's syrupy phosphoric acid have shown that phosphoric acid obtained from Albright and Wilson is quite satisfactory.

TABLE IV

Uranium^{VI} taken, *millimoles*	Uranium^{VI} found, *millimoles*
0·0725	0·0725
0·0925	0·0936
0·1050	0·1040
0·1125	0·1113
0·1250	0·1245
0·1507	0·1522
0·1758	0·1740

Procedure

About 4 to 8 ml of 0·025*M* uranyl salt solution is transferred to a titration vessel fitted with a five-holed stopper. These holes accommodate the inlet and outlet tubes for carbon dioxide, the platinum indicator electrode, the nozzle of the microburette containing the iron^{II} solution and one limb of the saturated potassium chloride bridge. The other limb of the bridge dips into a beaker containing saturated potassium chloride solution and this is connected to a saturated calomel electrode. From 30 to 65 ml of syrupy phosphoric acid is added to the titration vessel. The mixture is stirred by means of a Baird and Tatlock Ltd. magnetic stirrer, while the iron^{II} solution is run in from the burette. The e.m.f. of the cell is measured with the help of a Cambridge potentiometer and a Pye galvanometer. Electrometric titrations have been made using both a platinum wire electrode and a platinum gauze electrode. We have observed that the potentials attained stable values more easily with the platinum

wire electrode than with the platinum gauze electrode. Potential measurements were made 3 min after the addition of each instalment of titrant. Typical curves are given in Fig. 2. Some typical results from a large number of titrations are presented in Table IV.

Ferrometric Determination of Uranium^{VI} Using Methylene Blue and Thionine as Indicators

From the potentiometric titration curves the formal redox potentials of the U^{VI}/U^{IV} couple and the Fe^{III}/Fe^{II} couple can be computed to be 0·742 V* and 0·298 V*, respectively, in a medium containing phosphoric acid at a concentration of 13·1*M*. When the concentration of phosphoric acid is

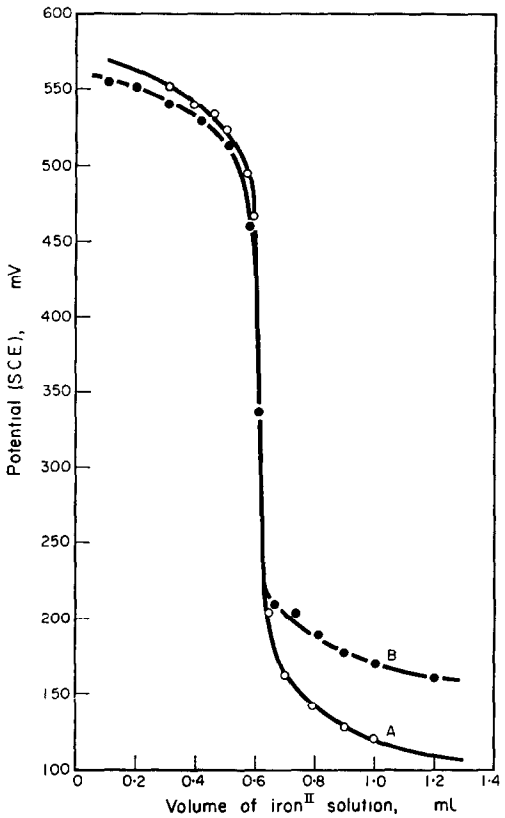


FIG. 2—Potentiometric titration of uranium^{VI} with iron^{II}
A—13·1*M* phosphoric acid,
B—11·6*M* phosphoric acid.

11·6*M*, the formal redox potentials of the two couples will be 0·73 V* and 0·35 V*, respectively. The difference in the potentials is sufficient for a direct titration to be made in media containing phosphoric acid at a concentration lying between 13·1 and 11·6*M*. Any redox indicator having a transition potential of about 0·5 to 0·6 V may work satisfactorily in the above titration. Hence, we have attempted to use methylene blue and thionine as redox indicators in this titration. The transition potentials of methylene blue and thionine have been found by the authors to be 0·550 V and 0·560 V in a medium containing phosphoric acid at 11·0–13·5*M*. The normal redox potentials for these indicators have been reported[13] to be 0·53 V and 0·56 V, respectively.

* These values may not correspond to the true equilibrium redox potentials of the U^{VI}/U^{IV} couple in view of the fact that the potentials have been taken after waiting for an arbitrary time interval of 3 min. Moreover, the potentials obtained during the titration are likely to be influenced by the presence of extraneous ions, *viz.* Fe^{3+} and Fe^{2+}. Similar considerations may also apply to the Fe^{III}/Fe^{II} couple.

Experiments made by us have shown that methylene blue and thionine are rapidly reduced by iron^{II} in an atmosphere free from oxygen in a concentrated phosphoric acid medium, even at concentrations of reactants obtaining near the close of a titration of uranium^{VI} with iron^{II}. We have also noticed that the oxidation of the leuco dye by uranium^{VI} is rather slow. Hence the two reactions important for the satisfactory functioning of the indicator can be represented as follows:

$$\underset{\text{(Dye)}}{D} + 2H^+ + 2Fe^{2+} \xrightarrow{H_3PO_4} \underset{\text{(Leuco dye)}}{DH_2} + 2Fe^{3+} \quad (1)$$

$$DH_2 + UO_2^{2+} + 2H^+ \xrightarrow{H_3PO_4} D + U^{4+} + 2H_2O \quad (2)$$

The fact that reaction (2) is slow and 'reaction (1) is fast' may make us believe that these dyes may not function satisfactorily as redox indicators in the reductimetric titration of uranium^{VI} with iron^{II} in a phosphoric acid medium. However, we made the interesting observation that the oxidation of leuco methylene blue by uranium^{VI} is induced by the fast reaction between iron^{II} and uranium^{VI}, so that the dyes can work satisfactorily as redox indicators.

In view of the above findings the authors have carried out the reductimetric titration of uranium^{VI} with iron^{II} using methylene blue as indicator in a medium containing phosphoric acid at a concentration not less than 11·6*M*. During such experiments it has been observed by the authors that in titrations containing small quantities of uranium (0·025 millimole of uranium per 50 ml), the colour change at the end-point is from blue to pale green or light green, this being the colour of uranium^{IV}. If the amount of uranium present in the solution is greater than 0·15 millimole for a final volume of 50 ml, the colour transition at the end-point is difficult to notice.

Reagents

Uranium^{VI} and iron^{II} solutions: Prepared and standardised as described above.

Methylene blue: A 0·1% aqueous solution of methylene blue prepared from the substance obtained from Dr. G. Grubler & Co., Leipzig, Germany.

When 0·5 ml of 0·1% methylene blue is used as indicator in titrations with 0·1*N* iron^{II} solution, the indicator correction has been found to be 0·02 ml. Hence this volume has to be deducted from the experimentally observed titres in order to get the correct values.

Thionine: A 0·1% aqueous solution of thionine prepared from a sample supplied by G. T. Gurr & Co., London, England.

Because leuco dyes are oxidised by air, the authors recommend that the titration of uranium^{VI} with iron^{II} using methylene blue and thionine as indicators be carried out in an atmosphere of carbon dioxide.

Procedure

An aliquot of uranium^{VI} containing less than 0·15 millimole of uranium and less than 5·0 ml in volume is transferred to a 100-ml beaker with the necessary arrangements already described. Forty-five ml of syrupy phosphoric acid and 0·5 ml of the dye solution are added and the mixture is kept well stirred with the magnetic paddle placed inside the mixture. Carbon dioxide is allowed to pass through the mixture. After 10 min, iron^{II} solution is added from a micro burette until the pale green or light green colour appearing at the end-point does not change to blue within 1 to 2 min. The amount of uranium present in the mixture is calculated after applying the necessary indicator correction. Some typical results obtained by the authors are given in Table V.

TABLE V

Methylene blue as redox indicator		Thionine as redox indicator	
Uranium^{VI} taken, *millimoles*	Uranium^{VI} found, *millimoles*	Uranium^{VI} taken, *millimoles*	Uranium^{VI} found, *millimoles*
0·0265	0·0267	0·0500	0·0503
0·0530	0·0533	0·0875	0·0870
0·0795	0·0790	0·1000	0·1005
0·1060	0·1060	0·1100	0·1100
0·1325	0·1320	0·1238	0·1231
0·1458	0·1450	0·1350	0·1353

Interferences

Iron^{III} and tungsten^{VI} have been found not to interfere with the accuracy of the determination of uranium^{VI} when the titration is carried out electrometrically. The presence of tungsten^{VI} is indeed beneficial as it helps a rapid attainment of stable potentials. This is the case even with higher amounts of tungstate although it gives a turbidity.

Vanadium^{V}, molybdenum^{VI} and chromium^{VI} interfere in the titration of uranium^{VI} with iron^{II} in a strong phosphoric acid medium. Further work is in progress.

Zusammenfassung—Die Formalpotentiale von Ferri/Ferro-Lösungen wurden in Gegenwart wechselnder Mengen von Phosphorsäure bestimmt; das Potential zeigt einen scharfen Abfall mit ansteigender Phosphatkonzentration. Oberhalb einer bestimmten Phosphorsäurekonzentration wird der Unterschied in den Formalpotentialen von U(VI)/U(IV) und Fe(III)/Fe(II) genügend gross, sodass Eisen(II) imstande is Uran(VI) selbst bei Zimmertemperatur zu reduzieren. Dies ist die Umkehr der üblichen Reaktion in der Uran(IV) durch Eisen(III) oxydiert wird. Eine Methode wurde ausgearbeitet um Uran(VI) in stark phosphorsaurem Medium (11–13·5 m) mit Eisen(II)-lösung zu titrieren. Die Endpunktsanzeige erfolgt entweder potentiometrisch oder visuell mittels Methylenblau oder Thionin. Die Methode is vorteilhaft, weil bei Raumtemperatur titriert wird und Uran(VI) in Gegenwart von Eisen(III) und Wolfram(VI) potentiometrisch bestimmt werden kann. Ein weiterer Vorteil ist, dass keine besonderen Vorkehrungen zur Lagerung der sonst üblicherweise verwendeten Titan(III) oder Chrom(II)-lösungen nötig sind.

Résumé—Les auteurs ont déterminé le potentiel normal apparent du couple fer(II)/fer(III) en milieu acide phosphorique de concentrations variées; ce potentiel décroît rapidement quand la concentration de l'acide phosphorique augmente. Au-dessus d'une certaine concentration d'acide phosphorique, la différence entre les potentiels normaux apparents des couples U(VI)/U(IV) et Fe(III)/Fe(II) devient suffisamment grande pour permettre la réduction de l'uranium (VI) par le fer(II) même à la température ambiante; cette réaction est l'inverse de la réction d'oxydo-réduction normale qui consiste en l'oxydation de l'uranium (IV) par le fer(III). Une étude soignée des différents facteurs mis en jeu a permis de mettre au point un nouveau titrage de l'uranium (VI) par le fer(II) en milieu acide phosphorique concentré (11,0 à 13,5 M) à la température ambiante; le point équivalent est déterminé par potentiométrie ou par colorimétrie en utilisant le-bleu de méthylène ou la thionine comme indicateur interne. Le nouveau procédé, permettant de réaliser le titrage à la température ambiante, est plus commode que les méthodes qui mettent en jeu le titane(III) et le chrome(II) et qui nécessitent des températures de 60 à 90°. Il possède un avantage supplémentaire: il peut être utilisé pour le dosage de l'uranium(VI) même en présence de fer (III) et de tungstène(VI) en déterminant le point équivalent par électrométrie. Enfin, il ne demande pas les précautions spéciales nécessaires pour la préparation et la conservation des solutions de titane(III) et de chrome(II).

REFERENCES

[1] R. G. Canning and P. Dixon, *Analyt. Chem.*, 1955, **24**, 877.
[2] C. F. Baes Jr., *J. Phys. Chem.*, 1956, **60**, 805.
[3] Y. Marcus, *ibid.*, 1958, **62**, 1314.
[4] I. M. Kolthoff and O. Tomicek, *Rec. Trav. Chim.*, 1924, **43**, 814.
[5] H. Steur, *Z. analyt. Chem.*, 1940, **118**, 386.
[6] J. Minczewski, R. Przytycka and L. Kohman, *Chem. Analit.*, 1958, **3**, 27; *Analyt. Abs.*, 1960, 7, 978.
[7] J. J. Lingane and R. T. Iwamoto, *Analyt. Chim. Acta*, 1955, **13**, 465.
[8] R. Flatt and F. Sommer, *Helv. Chim. Acta*, 1944, **27**, 1518.
[9] H. K. El-Shamy and S. Ed-Din Zayan, *Analyst*, 1955, **80**, 65.
[10] V. Panduranga Rao, B. V. S. R. Murty and G. Gopala Rao, *Z. analyt. Chem.*, 1956, **150**, 401.
[11] W. C. Schumb, M. S. Scherrill and S. B. Sweetser, *J. Amer. Chem. Soc.*, 1937, **59**, 2360.
[12] L. J. Andrews, W. B. Schaap and J. W. Gates Jr., Report CD 4014, Apr. 11, 1945; *cf.* C. J. Rodden, *Analytical Chemistry of the Manhattan Project*. McGraw-Hill Book Co., Inc. 1950, p. 78.
[13] O. Tomicek, *Chemical Indicators*. Butterworths Scientific Publications, 1951, p. 181.
[14] Linga Murty, M.Sc. thesis, 1955–56, Andhra University.

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PRELIMINARY COMMUNICATION

The hydrolysis of 8-acetoxyquinoline

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8-HYDROXYQUINOLINE has been widely used as a precipitant for certain metallic ions and its *in situ* generation by the hydrolysis of its acetate ester in buffered media has been employed for precipitation from homogeneous solution.[1,2,3,4,5,6] Because the rate of this hydrolysis is an important factor in the success of this technique, a study of some of the factors which affect the rate has been undertaken. The data obtained might also suggest a possible mechanism for the hydrolysis of this compound in which the structural relationship of the ester group and the basic ring nitrogen is rather unique. The rate of hydrolysis of 7-acetoxyquinoline had been determined under similar conditions in order to provide a basis for comparisons.

The hydrolysis of these esters at 35° in buffered solutions over a pH range of from 0 to 10 has been followed by means of spectrophotometric measurements in the ultraviolet region. The reaction was found to be first order with respect to the ester in this range and the rates, as calculated from the first order plots, found to be highly pH sensitive. The results of these measurements are summarised in Fig. 1.

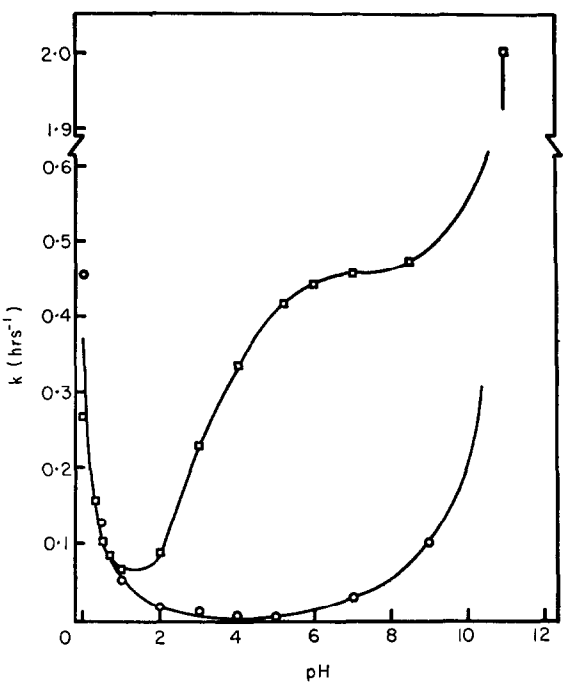


FIG. 1. Effect of pH on the first order rate constant: □—8-acetoxyquinoline, ○—7-acetoxyquinoline. Note the discontinuity in the ordinate.

From these data it is readily apparent that the selection of the correct pH is an important factor in evolving an effective procedure for precipitation from homogeneous solution. Although the effect of temperature upon this reaction has not been investigated, a first approximation would be that

increased temperature would not appreciably alter the shape of the rate *vs.* pH curve. With this assumption it is possible to estimate the effect that changes in acidity will have on rates of precipitation at the higher temperatures employed in such procedures.

A difference in the behaviour of the two esters in the pH range between 2 and 10 is quite evident, and it is suggested that this difference is probably caused by the formation of an intramolecular hydrogen bond between the nitrogen and the ester group in the case of the 8-acetoxyquinoline. This chelation, which is impossible with the 7-isomer, may catalyse the hydrolysis of the 8-acetoxyquinoline by stabilising the intermediate whose formation is the rate-limiting step. Further investigation is under way to confirm or refute the postulated mechanism, to study the effects of the presence of metallic cations, and to determine the changes induced by changing temperatures. A report of this current work and a more thorough description of the experimental techniques will be made at a later date.

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Summary—The rates of hydrolysis of 7-acetoxyquinoline and 8-acetoxyquinoline at 35° have been measured and are reported for the pH region from 0 to 10.

Zusammenfassung—Die Hydrolysegeschwindigkeiten von 7-acetoxychinolin und 8-acetoxychinolin wurden bei 35°C gemessen und werden für den pH-Bereich 0–10 mitgeteilt.

Résumé—Les auteurs ont mesuré les vitesses d'hydrolyse de la 7-acétoxyquinoléine et de la 8-acétoxyquinoléine à 35° et donné les valeurs obtenues pour le domaine de pH: 0–10.

REFERENCES

[1] J. Bordner, E. D. Salesin and L. Gordon, *Talanta*, 1961, **8**, 579.
[2] J. T. Corkins, R. F. Pietrzak and L. Gordon, *ibid.*, 1962, **9**, 49.
[3] L. C. Howick and W. W. Trigg, *Analyt. Chem.*, 1961, **33**, 302.
[4] D. J. Marec, E. D. Salesin and L. Gordon, *Talanta*, 1961, **8**, 293.
[5] E. D. Salesin and L. Gordon, *ibid.*, 1960, **4**, 75.
[6] K. Takiyama, E. D. Salesin and L. Gordon, *ibid.*, 1960, **5**, 231.

Talanta, 1962, Vol. 9, pp. 725 to 738. Pergamon Press Ltd. Printed in Northern Ireland

SHORT COMMUNICATIONS

Spot test for bivalent sulphur based on pyrolysis with mercuric cyanide*

(*Received* 25 *January* 1962. *Accepted* 30 *January* 1962)

STUDIES of pyrolysis reactions of mercuric cyanide with inorganic and organic compounds at temperatures up to 180° included an investigation of the behaviour of elementary sulphur. Because of the marked affinity between sulphur and mercury, and also because of the ease with which mercuric cyanide breaks down when heated, according to the reaction:

$$Hg(CN)_2 \rightarrow Hg^\circ + (CN)_2,$$

it was only natural to expect the occurrence of the reaction

$$S^\circ + Hg(CN)_2 \rightarrow HgS + (CN)_2.$$

Trials showed that black mercuric sulphide did in fact appear very quickly, but dicyanogen was not produced since no response was given for this volatile compound when the extremely sensitive test with alkali cyanide and 8-hydroxyquinoline (red colour[1]) was applied. In contrast, when a disc of filter paper moistened with copper acetate-benzidine acetate was held above the heated reaction mixture, the paper turned blue, a reaction characteristic of hydrogen cyanide.[2] Because the formation of mercuric sulphide and hydrogen cyanide is known to occur even during the dry heating of mercuric thiocyanate, the pyrolysis of mercuric cyanide with sulphur may involve the formation and thermal decomposition of mercuric thiocyanate. The formation doubtless occurs through the addition reaction:

$$2S + Hg(CN)_2 \rightarrow Hg(CNS)_2.$$

The formation of mercuric sulphide points to fission of mercuric thiocyanate by thermal decomposition, leading to dicyanogen sulphide:

$$Hg(CNS)_2 \rightarrow HgS + (CN)_2S \qquad (1)$$

Dicyanogen sulphide has been prepared by other procedures and has been described[3] as a compound which sublimes appreciably at 30°-40° and melts at 60°. Furthermore, when dissolved in water it decomposes with formation of hydrogen cyanide. Therefore we assume that the positive response to the hydrogen cyanide colour reaction, when the $(CN)_2S$ vapours come into contact with the moist reagent paper, results from a hydrolysis leading to hydrogen cyanide, with participation of atmospheric oxygen. The following reactions may be involved:

$$(CN)_2S + H_2O \rightarrow HCN + HCNSO \qquad (2)$$

$$(CN)_2S + H_2O + O \rightarrow 2\,HCN + SO_2 \qquad (2a)$$

Evidence for the occurrence of reaction (2a) is furnished by the fact that the vapours evolved during the dry heating of mercuric thiocyanate, or a mixture of mercury cyanide and sulphur, give the colour reaction characteristic of sulphur dioxide (blue colour on Congo paper moistened with H_2O_2 or on filter paper moistened with $Fe[Fe(CN)_6]$ solution.[4]

It has now been found that alkali thiocyanates and organic thiocyanates behave in the same manner as elementary sulphur when pyrolysed with mercuric cyanide. Obviously, these compounds break down thus:

$$2\,KCNS + Hg(CN)_2 \rightarrow Hg(CNS)_2 + 2\,KCN$$

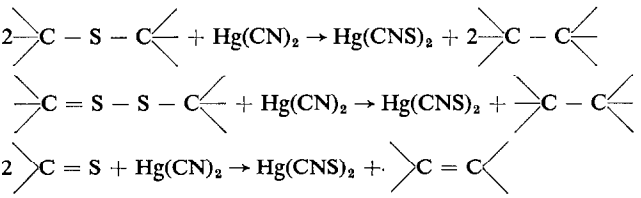
$$2\,R(Ar)CNS + Hg(CN)_2 \rightarrow Hg(CNS)_2 + 2\,R(Ar)CN$$

and reactions 1, 2, and 2a may then occur.

The removal of sulphur from organic thiocyanates is readily detected by the hydrogen cyanide colour reaction. Since these compounds contain bivalent sulphur in the SCN group, it could be

* Translated by Ralph E. Oesper, University of Cincinnati, U.S.A.

expected[5] that other organic compounds containing bivalent sulphur would react in an analogous fashion. This expectation is confirmed in the case of open and cyclic thioethers, aliphatic and aromatic disulphides, and thioketones. We suggest that the following 'pyrolytic reactions lead to the formation of mercuric thiocyanate:



The above desulphurisations, which patently are a consequence of the marked tendency of mercuric thiocyanate to form, make possible (in combination with reactions 1, 2, and 2a), the detection of compounds of these types; they may also be of interest from the viewpoint of preparative organic chemistry in cases where the course of the reactions postulated here applies.

Organic compounds containing bivalent sulphur include not only sulphides, disulphides and thioketones but also thiols. This last group reacts (in the wet way) with mercuric cyanide through the acidic SH group, with formation of hydrogen cyanide:

$$2\ R(Ar)SH + Hg(CN)_2 \rightarrow [R(Ar)S]_2Hg + 2\ HCN$$

Accordingly, the production of hydrogen cyanide during the pyrolytic action with mercuric cyanide may be utilised as a preliminary test for bivalent sulphur in organic compounds. A necessary condition is the absence of acidic compounds which likewise yield hydrogen cyanide when dry-heated with mercuric cyanide.* However, in the majority of instances, sulphides, disulphides and thioketones can be separated from acidic compounds (including thiols) by shaking the sample in alkaline medium with chloroform or ether. The alkali salts of the acidic compounds remain in the water layer.

Neutral compounds containing quadrivalent sulphur do not react with mercuric cyanide. For instance, alkali salts of sulphinic acids were tested, with negative results.

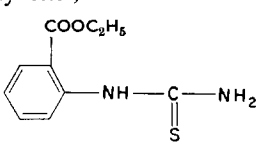
Trials were made to learn how elementary selenium and organic compounds containing bivalent selenium behave when pyrolysed with mercuric cyanide. Since black mercuric selenide results, the likelihood is that the initial product is mercuric selenocyanide, which then thermally decomposes to yield dicyanoselenide. The latter also produces hydrogen cyanide on hydrolysis. Therefore the test for bivalent sulphur as described here, by pyrolysis with mercuric cyanide, is reliable only in the absence of organic compounds containing bivalent selenium. The presence or absence of selenium can be recognised simply by means of a recently described spot test.[6]

Procedure: A micro test-tube is used. A small amount of the solid test material, or of the evaporation residue from 1 drop of a benzene solution, is stirred with several cg of mercuric cyanide using a dry glass rod. A drop of acetone is added and volatilised. The test-tube is immersed to a depth of about 0·5 cm in a glycerol bath preheated to 120°, and the open end is covered with a piece of filter paper moistened with hydrogen cyanide reagent. The temperature is raised to 180°. Development of a blue stain on the reagent paper indicates a positive test.

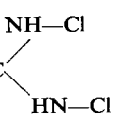
Hydrogen cyanide reagent (*copper acetate-benzidine acetate solution*). The preparation of this reagent solution is described in detail elsewhere, ref 5, p. 366.

Limits of identification:

10 μg *o*-carboxyphenylthiourea, ethyl ester,



10 μg *N,N'*-dichlorothiourea,



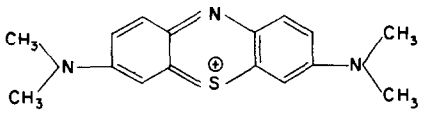
$C_{10}H_7$—NH—C—NH_2.

* It has been found that a test for such materials can be based on this reaction.

10 μg naphthylthiourea,

5 μg 4,4′-bis(dimethylamino)thiobenzophenone, $[(CH_3)_2NC_6H_4]_2$ CS.

50 μg thiocarbanilide $C_6H_5NH—CS—NHC_6H_5$.

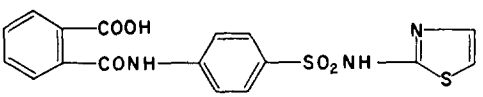


10 μg methylene blue;

5 μg *l*-cystine, $[—SCH_2CH(NH_2)COOH]_2$.

5 μg phthalylsulphathiazole,

5 μg dithio-oxamide, $NH_2CSCSNH_2$.



Summary—The test described for bivalent sulphur in organic compounds is based on the finding that hydrogen cyanide can be detected in the gas phase if the sample is heated with mercuric cyanide to 180°. The identification limits range from 5 to 50 μg. An explanation is advanced for the chemistry of the pyrolytic reaction.

Zusammenfassung—Es wird ein Nachweis von 2-wertigem Schwefel in organischen Verbindungen beschrieben, der darauf veruht dass bei trockener Erhitzung (180° C.) mit Quecksilberzyanid in der Gasphase Cyanwasserstoff nachzuweisen ist. In der Arbeitsweise der Tüpfelanalyse werden Erfassungsgrenzen von 5-50 μg erhalten. Für den Chemismus der pyrolytischen Umsetzung kann eine plausible Erklärung gegeben werden.

Résumé—Les auteurs décrivent une recherche du soufre au degré d'oxydation + 2 dans les composés organiques; cette recherche est basée sur le fait qu'on peut déceler de l'acide cyanhydrique en phase gazeuse si l'échantillon est chauffé à 180° C avec du cyanure mercurique. Les limites d'identification vont de 5 à 50 μg. Une explication plausible peut être suggérée pour la chimie de la réaction pyrolytique.

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REFERENCES

[1] F. Feigl and L. Hainberger, *Analyst*, 1955, **80**, 807.
[2] A. Sieverts and A. Hermsdorf, *Angew. Chem.*, 1921, **34**, 3.
[3] *cf.* Beilstein, *Handbuch d.org. Chemie*, Vol. III, Berlin, 1921, p. 180.
[4] G. B. Heisig and A. Lerner, *Ind. Eng. Chem., Analyt.*, 1941, **13**, 843.
[5] F. Feigl, *Analyt. chim. Acta*, 1960, **24**, 501.

Contribution to the analytical use of a standard solution of iodine trichloride

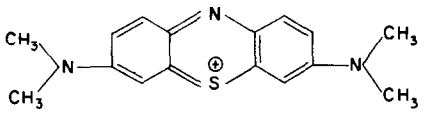
(*Received* 23 *November* 1961. *Accepted* 8 *March* 1962)

THE analytical use of hydrochloric acid solutions of iodine monochloride and of iodine trichloride as standard solutions—"iodine-chlorometry"—was first suggested by Gengrinovich and coworkers.[1,2]

10 μg naphthylthiourea,

5 μg 4,4′-bis(dimethylamino)thiobenzophenone, $[(CH_3)_2NC_6H_4]_2$ CS.

50 μg thiocarbanilide $C_6H_5NH—CS—NHC_6H_5$.

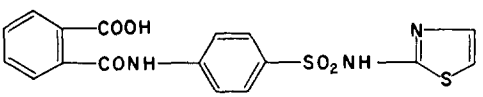


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REFERENCES

[1] F. Feigl and L. Hainberger, *Analyst*, 1955, **80**, 807.
[2] A. Sieverts and A. Hermsdorf, *Angew. Chem.*, 1921, **34**, 3.
[3] *cf.* Beilstein, *Handbuch d.org. Chemie*, Vol. III, Berlin, 1921, p. 180.
[4] G. B. Heisig and A. Lerner, *Ind. Eng. Chem., Analyt.*, 1941, **13**, 843.
[5] F. Feigl, *Analyt. chim. Acta*, 1960, **24**, 501.

Contribution to the analytical use of a standard solution of iodine trichloride

(*Received* 23 *November* 1961. *Accepted* 8 *March* 1962)

THE analytical use of hydrochloric acid solutions of iodine monochloride and of iodine trichloride as standard solutions—"iodine-chlorometry"—was first suggested by Gengrinovich and coworkers.[1,2]

A 0·1*N* standard solution of iodine trichloride was prepared from equivalent amounts of potassium iodide and potassium iodate with the use of hydrochloric acid, according to the equation:

$$KI + 2KIO_3 + 12HCl \rightarrow 3ICl_3 + 3KCl + 6H_2O \quad (1)$$

The resulting solution, about 0·5*N* with respect to hydrochloric acid, was found to be suitable for solving a number of analytical problems.[3,4,5,6,7,8,9]

According to the above authors,[2] the following equilibria exist in the solution of iodine trichloride:

$$ICl_3 + HCl \rightleftharpoons HICl_4 \quad (2a)$$

$$HICl_4 \rightleftharpoons H^+ + ICl_4^- \quad (2b)$$

$$ICl_4^- \rightleftharpoons ICl_2^- + Cl_2 \quad (2c)$$

The different types of reaction of iodine trichloride were interpreted by these authors on the basis of (2a), (2b) and (2c).

However, on considering the results of our experiments conducted with hydrochloric acid solutions of iodine trichloride from quite different aspects,[10] the existence of equilibria of the type shown does not seem probable. In order to clarify the situation, the following experiments were carried out.

The absorption curves of a 0·01*N* standard solution of "iodine trichloride"* (prepared from 0·1*N* iodine trichloride standard solution by dilution with 0·5*N* hydrochloric acid) and of a 0·01*N* standard solution of iodine monochloride (prepared from 0·1*N* iodine monochloride standard solution by dilution with 0·5*N* hydrochloric acid) were established.

In both cases regular curves, characteristic of the chloride complex of iodine monochloride, were obtained. However, differences appeared in the values of the extinctions measured at the site of the maximum (343 mμ). Namely, the extinction value of the 0·01*N* solution of iodine monochloride was exactly the quadruple of that of the 0·01*N* solution of "iodine trichloride". This points to the fact that 25% of the full oxidation power of the "iodine trichloride" actually originates from iodine monochloride. According to its spectrum the solution contains no elementary iodine, so that the residual 75% of the oxidation power might be ascribed to elementary chlorine or iodate or eventually to both of them.

The accurate composition of the standard solution of "iodine trichloride" was established in the following manner.

1. In order to determine the chlorine content of the solution, an aliquot was treated with potassium cyanide solution which had been previously neutralised with hydrochloric acid. The oxidising power of the mixture was then determined iodometrically. The value agreed with the "full" oxidising power.†

From (2c), the full oxidising power is given by:

$$Cl_2 + 2I^- \rightarrow I_2 + 2Cl^-.$$

$$ICl_2^- + I^- \rightarrow I_2 + 2Cl^-.$$

However, if potassium cyanide is added first:

$$Cl_2 + CN^- \rightarrow ClCN + Cl^- \text{ (see reference 11)}$$

$$ICl_2^- + CN^- \rightarrow ICN + 2Cl^- \text{ (see reference 12)}$$

which is followed by:

$$ICN + I^- + H^+ \rightarrow I_2 + HCN$$

since cyanogen chloride is inactive iodometrically. The fact that no decrease in the oxidation power occurs after treatment with potassium cyanide [a 50% decrease would be expected on the basis of (2c)] proves that the solution contains no elementary chlorine. Because iodate does not react with cyanide ion, the effect on the oxidation power of any iodate present in solution would be unchanged after adding potassium cyanide.

2. In order to determine the iodate content of the solution, an aliquot was treated with potassium cyanide and sodium hydroxide, then warmed. The oxidising power of this solution was determined iodometrically and found to be 75% of the "full "oxidising power.

Assuming the chloride complex of iodine monochloride and iodate to be present in the original solution, the full oxidising power is given by:

$$ICl_2^- + I^- \rightarrow I_2 + 2Cl^-$$

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O.$$

* Quotation marks are used because, as will be proved later, no iodine trichloride or only traces of it are actually present in the standard solution.

† The oxidising power determined without adding potassium cyanide.

However, if potassium cyanide is added first (iodate does not react with cyanide ion) and warmed with sodium hydroxide:

$$ICl_2^- + CN^- \rightarrow ICN + 2Cl^-$$

$$ICN + OH^- \rightarrow I^- + CNO^- + H^+$$

which is followed by:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O.$$

Consequently, from the aspect of oxidation power, a standard solution of "iodine trichloride" presumably contains equimolecular amounts of iodate and iodine monochloride.

The experiments described above under 1 and 2 were repeated with a 0·1*N* solution of tetrachlorohydriodic acid (pure crystalline $HICl_4 \cdot 4H_2O$ was prepared and dissolved in 0·5*N* hydrochloric acid). The absorption curve of this solution diluted to 0·01*N* with 0·5*N* hydrochloric acid was also established. The data obtained from these experiments supported the conclusion that "iodine trichloride" solution contains equal amounts of iodate and iodine monochloride.

On the basis of our results, the following overall conversion presumably takes place in a standard solution of iodine trichloride which is about 0·5*N* with respect to hydrochloric acid, immediately after its preparation:

$$2ICl_3 + 3H_2O \rightleftharpoons ICl + HIO_3 + 5HCl \qquad (3)$$

Our investigations with respect to the mechanism of this reaction will be published elsewhere.[10]

In terms of the above knowledge of a 0·1*N* standard solution of iodine trichloride in hydrochloric acid it is readily possible to interpret both the oxidation and the addition and halogen substitution reactions of the solution. It appears unnecessary to interpret oxidation reactions separately. In substitution and addition reactions, iodine monochloride participates by saturating the olefinic bond and substituting the aromatic ring, respectively. The residual iodate, together with the excess of standard solution is measured iodometrically. (According to Gengrinovich[1] one actually measures excess standard solution and chlorine on back titration.)

Obviously there is no objection against the further use of analytical methods connected with a standard solution of "iodine trichloride" or of the conventional equivalent weights [*cf.* (2c) and (3)]. It is, however, preferable to use standard solutions of bromine chloride and iodine monochloride, respectively, in oxidation, in addition or in halogen substitution reactions.

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Summary—In order to establish its accurate composition, the 0·1*N* standard solution of iodine trichloride suggested by Gengrinovich has been subjected to re-investigation. It was found that iodate is responsible for 75% and iodine monochloride for 25% of the total oxidation power of the solution. The presence of iodine trichloride could not be detected. In terms of this knowledge of the exact composition of the solution it is possible to consider in an entirely new way the chemical reactions occurring during its use.

Zusammenfassung—Um die richtige Zusammensetzung der von Gengrinovich als Massflüssigkeit empfohlenen 0,1*N* Jodtrichloridlösung haben die Verfasser Versuche ausgeführt. Es wurde festgestellt, dass 75% des totalen Oxidierungswertes der Masslösung dem infolge Hydrolyse des Jodtrichlorids entstandenen Jodat-Ion und 25% des Oxidierungswertes dem Jodmonochlorid ($2JCl_3 + 3H_2O \rightarrow FCl + HJO_3 + 5HCl$) zuzuschreiben ist. Die Anwesenheit von JCl_3 konnte weder auf fotometrischem Wege (u.v.), noch mit chemischen Methoden nachgewiesen werden

Résumé—Les auteurs ont étudié la solution standard 0,1*N* de trichlorure d'iode suggérée par Gengrinovich, afin d'établir sa composition précise. Ils trouvèrent que l'iodate est responsable de 75% des propriétés oxydantes de la solution et le monochlorure d'iode de 25%. La présence de trichlorure d'iode n'a pas pu être décelée dans la solution. Pour connaître la composition exacte de la solution, les auteurs ont pu considérer d'une manière tout à fait nouvelle les réactions chimiques qui se produisaient pendant son utilisation.

REFERENCES

[1] A. I. Gengrinovich, *Ukrain. pharm. Zhur.*, 1940, **2**, 27.
[2] A. I. Gengrinovich, F. E. Kagan and Y. A. Fialkov, *Trudy Kom. analit. Khim.* Tom. V/VIII/1954, 237.
[3] Y. A. Fialkov and F. E. Kagan, *Ukrain. khim. Zhur.*, 1952, **18**, 55.
[4] *Idem, Zhur. obshchei Khim.*, 1954, **24**, 3.
[5] F. E. Kagan, *Aptechnoe delo B.*, 1957, **1**, 14.
[6] Y. A. Fialkov and F. E. Kagan, *Ukrain. khim. Zhur.*, 1952, **18**, 64.
[7] F. E. Kagan, *ibid.*, 1956, **22**, 44, 95.
[8] C. Y. Shakh, *Aptechnoe delo B.*, 1957, **1**, 22.
[9] Y. A. Fialkov, F. E. Kagan, *Zhur. obshchei Khim.*, 1957, **27**, 2836.
[10] E. Schulek, K. Burger and L. Ladányi, *Acta Chim. Acad. Sci. Hung.*, in press.
[11] E. Schulek, *Analyt. Chim. Acta*, 1948, **2**, 74.
[12] J. Cornog, H. W. Horrabin and R. A. Karges, *J. Amer. Chem. Soc.*, 1938, **60**, 429.

Chelating action of thioglycollic acid with silver and some common bivalent cations

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THIOGLYCOLLIC acid has been much used as a colorimetric agent for the spectrophotometric determination of iron^{III} with which it forms a soluble red product in ammoniacal solution. The constitution of this complex has been reported variously as $Fe(OH)\cdot(SCH_2COO)_2^{2-}$,[1] $Fe(SCH_2COO)_2^{1-}$,[2] and $[Fe(SCH_2COO)_2]_2KFe$.[3] Thioglycollic acid forms precipitates or soluble coloured compounds with many ions, *e.g.*, bismuth, cobalt, nickel, lead, mercury^{I}, uranium^{VI}, manganese and gold, but has been said not to react with aluminium, barium, calcium, strontium, chromium and zinc.[4] More recently, however, it has been shown that in alkaline solution the soluble colourless complexes of thioglycollic acid with lead, bismuth, cadmium, silver, mercury^{II}, zinc, thallium^{III}, indium and tin, are stronger than the EDTA complexes of these metals.[5] Thioglycollic acid therefore serves as a useful masking agent in complexometric titrations with EDTA and can be used in place of potassium cyanide in many determinations. Thioglycollic acid has also been used in the extractive determination of molybdenum.[6]

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REFERENCES

[1] A. I. Gengrinovich, *Ukrain. pharm. Zhur.*, 1940, **2**, 27.
[2] A. I. Gengrinovich, F. E. Kagan and Y. A. Fialkov, *Trudy Kom. analit. Khim.* Tom. V/VIII/1954, 237.
[3] Y. A. Fialkov and F. E. Kagan, *Ukrain. khim. Zhur.*, 1952, **18**, 55.
[4] *Idem, Zhur. obshchei Khim.*, 1954, **24**, 3.
[5] F. E. Kagan, *Aptechnoe delo B.*, 1957, **1**, 14.
[6] Y. A. Fialkov and F. E. Kagan, *Ukrain. khim. Zhur.*, 1952, **18**, 64.
[7] F. E. Kagan, *ibid.*, 1956, **22**, 44, 95.
[8] C. Y. Shakh, *Aptechnoe delo B.*, 1957, **1**, 22.
[9] Y. A. Fialkov, F. E. Kagan, *Zhur. obshchei Khim.*, 1957, **27**, 2836.
[10] E. Schulek, K. Burger and L. Ladányi, *Acta Chim. Acad. Sci. Hung.*, in press.
[11] E. Schulek, *Analyt. Chim. Acta*, 1948, **2**, 74.
[12] J. Cornog, H. W. Horrabin and R. A. Karges, *J. Amer. Chem. Soc.*, 1938, **60**, 429.

Chelating action of thioglycollic acid with silver and some common bivalent cations

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Zinc. Zinc was titrated directly with TGA at the 0·1*M* level with Solochrome Black T as indicator at pH 10 in an ammonia buffer. The quality of the end-point was poor because of attack by TGA on the indicator. Optimum conditions were obtained by adding the indicator only near the end-point. Clear indication of a highly soluble $Zn(SCH_2COO)_3^{4-}$ complex was obtained. A very precise end-point was obtained by the back-titration process with EDTA and the same indicator-buffer system. Once more, clear evidence was obtained of a 1:3 complex. Such a complex could presumably be formed readily at pH by addition of another TGA molecule to the $Zn(SCH_2COO)_2^{2-}$ complex previously reported by others. In fact Leussing comments that the remaining co-ordination sites on the

zinc ion in the 1:2 complex are probably occupied by water molecules. However, under our conditions at least, there is very precise definition of the 1:3 complex and we find no stereochemical reason for non-formation of such a complex.

Mercury^{II}. Mercury was titrated with TGA at pH 6 in a pyridine acetate buffer. A precipitate was formed initially, then dissolved sharply near the end-point. Xylenol Orange was used as indicator, but the disappearance of the colloidal precipitate at equivalence gave a clear indication of the nearness of the end-point. The mechanism of this particular reaction is of considerable interest. The $Hg_2(SCH_2COO)_2$ insoluble compound postulated by earlier workers may well account for the initial formation of the precipitate observed by us in the initial stages of the titration where an excess of mercury^{II} ions would further repress its solubility. Furthermore, the removal of free mercury^{II} ions by TGA at equivalence (1:1) would account for the disappearance of turbidity and the near simultaneous colour change of the indicator is to be expected because the 1:1 complex may be assumed to be sufficiently associated not to affect visibly the Xylenol Orange indicator. Thus the existence of the $Hg(SCH_2COO)_2^{2-}$ complex reported by Kolthoff and his coworkers would not be in evidence here for the reasons noted above.

A 1:1 complex was also found in the second series of experiments when an excess of mercury^{II} was added to TGA and the excess back-titrated with EDTA using the Xylenol Orange indicator and pyridine buffer system. Here once more we would not expect experimental evidence for the formation of anything other than the 1:1 complex because the latter is obviously more stable than the mercury^{II}-EDTA complex under these conditions. Both procedures therefore confirm the existence of the 1:1 complex which was previously reported by Kolthoff *et al.*[9] and assigned a binuclear structure by them.

Cadmium. Cadmium was titrated directly with TGA in an ammonia buffer at pH 10 with Solochrome Black 6B as indicator. Solochrome Black T and Catechol Violet were also examined as indicators, but the first mentioned was preferred. As with zinc, difficulties were once more experienced because of attack on the indicator. Despite this, however, consistently reproducible results were obtained which indicated the formation of a highly soluble $Cd_2(SCH_2COO)_3^{2-}$ complex. Similarly, when an excess of cadmium^{II} ions was added to TGA and the excess was back-titrated with EDTA using the same indicator-buffer system once more, a clear indication of a 2:3 complex was obtained. Other workers have avoided definition of the cadmium complex probably because similar results obtained by them did not fit in with the usual 1:2 ratio pattern for all other ions which had been examined previously.

Lead. Lead was titrated directly with TGA in a manner similar to zinc and cadmium. As before, a rather poor end-point was obtained, but in this instance the evidence pointed to the formation of a $Pb(SCH_2COO)_2^{2-}$ complex. A back titration process with EDTA as above also gave a reaction ratio Pb:TGA = 1:2. This result agrees well with the 1:2 complexes previously reported for nickel^{II}, iron^{II}, cobalt^{II} and manganese^{II}.

Silver. There is a lack of metallochromic indicators for silver ion, but it was found possible to detect the end-point with *p*-dimethylaminobenzalrhodanine. The end-point was quite sharply defined though the colour contrast was poor. The addition of Xylene Cyanol F.F. improved the colour change in ammoniacal solution and the direct titration was readily effected with precise indication of an $Ag(SCH_2COO)^-$ complex. It was not possible to carry out a back-titration in this instance because of the low stability constant of the silver-EDTA chelate. However, potentiometric titration with a silver-metal indicator electrode was performed successfully. This also gave unequivocal evidence of a 1:1 complex. The silver complex does not appear to have been formulated previously.

Homologues of thioglycollic acid and allied reagents

As a matter of general interest some additional titrations of silver were carried out potentiometrically with β-mercaptopropionic acid, β-mercaptosuccinic acid and thiodiglycol. Since we were not concerned with quantitative data here, the technical acids, which were the only materials available to us, were used for the preparation of these reagents and no purification or standardisation was attempted. The potentiometric curves obtained with these reagents are compared with that of thioglycollic acid in Fig. 1. As expected, β-mercaptopropionic acid behaved in a manner similar to thioglycollic acid whilst thiodiglycol, which contains no active mercapto-group, showed no complexing action. The β-mercaptosuccinic acid curve shows fairly definite evidence of a 2:1 as well as a 1:1 silver: reagent complex. This work was not pursued further, however, because these reagents offer no particular advantages for analytical purposes, which was the aspect of this study of immediate interest to us at the time.

DISCUSSION

The foregoing study has established the empirical formulae of some complexes of bivalent metal ions with thioglycollic acid, mainly in an ammoniacal medium where it was proposed to use the complexing action of TGA for complexometric titration purposes. In no case, however, has the reagent

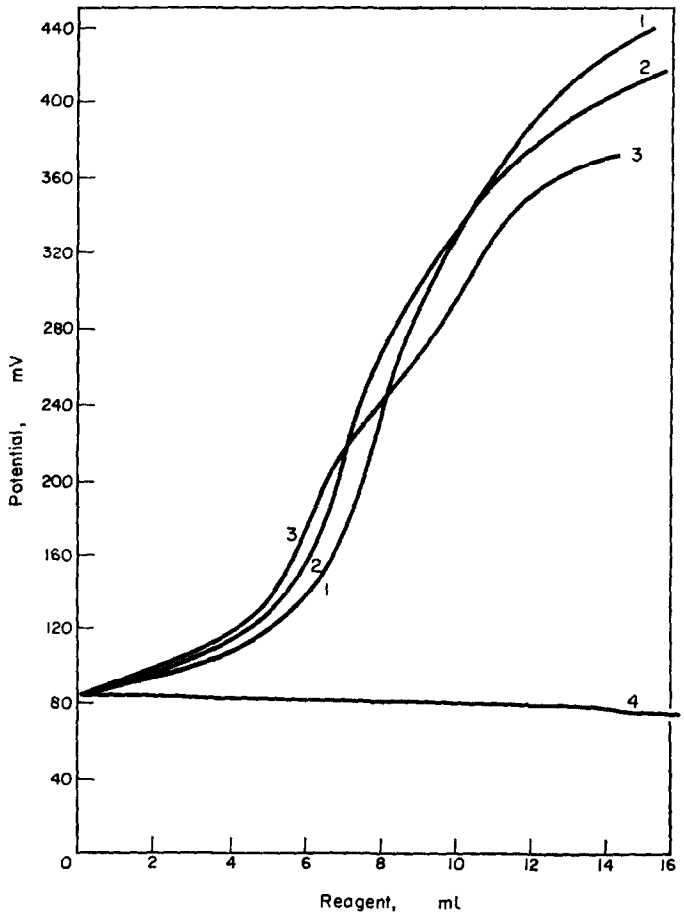


FIG. 1—Potentiometric titration of 10 ml of 0·1*M* silver nitrate in ammoniacal solution (silver-metal/calomel electrode system):.
1—1% β-mercaptopropionic acid,
2—1% thioglycollic acid,
3—1·5% β-mercaptosuccinic acid,
4—1·2% thiodiglycol.

been found to possess sufficient advantage over conventional methods with ethylenediaminetetra-acetic acid except that a direct complexometric titration of silver may be possible though with a poorly defined visual end-point. The potentiometric end-point for silver is fairly well defined, but in this respect it may be stated that the end-points obtained when cyanide ion or chloride ion are used are probably superior.

We have obtained good results for the analysis of chlorides, bromides and iodides by dissolving these halide precipitates of silver in an excess of ammoniacal TGA and back-titration to a potentiometric or *p*-dimethylaminobenzalrhodanine end-point, but once more the lack of a more suitable visual indicator militates against the adoption of such a procedure.

An aqueous 1% solution of TGA stored in a well-stoppered brown bottle is not markedly unstable, and our evidence is that after 14 days, during which time the bottle was opened *ca.* once per 2 days, the equivalence of the solution was still 90% of its original value, when freshly prepared. No perceptible decrease in strength of the reagent solution was observed over the first 24 hr, though it is possible that considerable differences for stability could be obtained depending on the manner of storage and frequency of opening the vessel, *etc.*

Acknowledgements—We are grateful to Professor F. Burriel-Marti of the University of Madrid, Spain, for granting study leave to one of us (A. M. C.) and to the Spanish High Council for Scientific Research for the provision of a research grant. We also wish to thank Professor R. Belcher of this Department for his interest in the work.

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Summary—The reactions between thioglycollic acid and some bivalent cations, *viz.* zinc, mercury, cadmium, lead and more particularly with silver, are studied by direct and indirect complexometric titration. New complexes are reported with zinc, cadmium and lead, and the silver complex is also formulated. The potential use of the reagent as a complexometric titrant for silver ion is hindered by the lack of suitable metallochromic indicators.

Zusammenfassung—Die Reaktion zwischen Thioglycolsäure und einigen zweiwertigen Ionen (Zn, Hg, Cd, Pb) und im besonderen Silber wurde mittels direkter und indirekter komplexometrischer Titration studiert. Neue Komplexe mit Zn, Cd und Pb wurden nachgewiesen und der Silberkomplex wurde formuliert. Die Verwendung des Reagenses als komplexometrisches Titrationsmittel für Silber ist theoretisch möglich, scheitert aber in Praxis am Fehlen eines geeigneten metallochromen Indicators.

Résumé—Les auteurs ont étudié, par titrage complexométrique direct et indirect, les réactions entre l'acide thioglycollique et quelques cations divalents: Zn, Hg, Cd, Pb et plus particulièrement Ag. De nouveaux complexes sont décrits dans le cas de Zn, Cd et Pb et une formule du complexe de Ag est donnée. L'utilisation du réactif comme agent de titrage complexométrique pour l'ion Ag est gênée par le manque de réactifs métallochromes convenables.

REFERENCES

[1] D. L. Leussing and I. M. Kolthoff, *J. Amer. Chem. Soc.*, 1953, **75**, 3904.
[2] S. Chaberek and A. E. Martell, *Organic Sequestering Agents*. J. Wiley and Sons, Inc., New York, 1959. p. 379 and references therein.
[3] C. Mayr and A. Gebauer, *Z. analyt. Chem.*, 1939, **116**, 225.
[4] I. Mellan, *Organic Reagents In Inorganic Analysis*. Blakiston Co., Philadelphia, 1941. p. 136 and references therein.
[5] R. Přibil and V. Veselý, *Talanta*, 1961, **8**, 880.
[6] M. Ziegler and H.-G. Horn, *Z. analyt. Chem.*, 1959, **166**, 362; M. Zeigler, O. Glemser and A. von Baeckmann, *Angew. Chem.*, 1958, **70**, 500.
[7] D. L. Leussing, *J. Amer. Chem. Soc.*, 1958, **80**, 4180.
[8] N. C. Li and R. A. Manning, *ibid.*, 1955, **77**, 5225.
[9] W. Stricks, I. M. Kolthoff and A. Heyndrickx, *ibid.*, 1954, **76**, 1515.

Phase titrations—I: Binary systems involving carbon tetrachloride and binary systems involving carbon disulphide

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THE technique of phase titration is not new. Siggia[1,2] mentions two component phase titrations, Bogin[3] and Spiridonova[4,5,6] have reported phase titrations and, recently, Caley and Habboush[7] reported the phase titration of 14 binary systems involving alcohols and aromatics, using water as the titrant. They give a discussion of errors which may arise and take detailed precautions to avoid them. In the present work, calibration curves were set up by titrating known solutions under the same conditions as unknowns, stressing, not the avoidance of error, but its cancellation. The result is a very

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rapid technique allowing as many as 15 to 20 titrations to be carried out in 1 hr, using the simplest apparatus and chemicals and sacrificing only a small degree of the accuracy inherent in phase titrations.

THEORY

When water is added to a homogeneous solution of two organic liquids, one of which is immiscible with water, a phase separation takes place and the solution becomes turbid. The amount of water which must be added to cause phase separation depends on the temperature of the system, the nature of the organic liquids and their relative amounts. A common method of determining the phase diagrams for systems of water and two organic liquids is phase titration with water to a turbidimetric end-point.[8] If the composition of several solutions is known, the phase diagram can be determined. Conversely, if the phase diagram is known, the composition of the original binary solution can be determined.

Phase diagrams

Ternary phase diagrams have been represented by equilateral triangles for many years.[9] Fig. 1 shows the phase diagram of a common type of ternary system, in which one pair of liquids is immiscible in all proportions and the other two are miscible in all proportions. The phase diagram for carbon

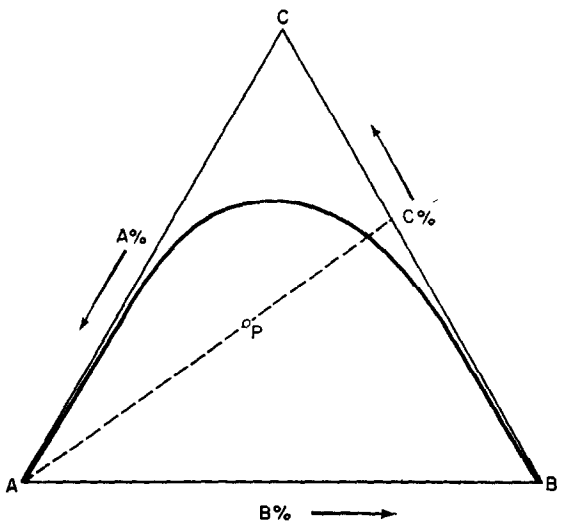


FIG. 1.—Representation of a three component system using an equilateral triangle. The dotted line represents the titration of a 40:60 binary solution of B to C with A. Point P represents the ternary solution with the composition 40% of A, 24% of B and 36% of C.

tetrachloride, ethanol and water[10] is one of many like Fig. 1. Systems represented by a point below the solubility curve (curved line within triangle) are heterogeneous and turbid.

A straight line from one apex, say A, to the opposite side is the locus of points representing a constant ratio of B to C and varying amounts of A. Such a line represents the titration of a binary mixture of B and C using A as the titrant. The intersection of the dotted titration line with the solubility curve is the composition at which the second phase separates and turbidity appears.

Phase Titrations

The phase titration of a 90:10 mixture of C to B with A follows line 1 in Fig. 2(a). Titrations of 80:20, 70:30, 60:40 and 50:50 mixtures of C to B follow lines 2 to 5. As the concentration of the immiscible component, B, becomes greater, the amount of A necessary to cause phase separation rapidly becomes smaller. The titre approaches infinity (complete miscibility with the titrant) as the original solution composition approaches pure C and zero (complete immiscibility) as the original solution composition approaches pure B.

If the volume (ml) of A necessary to cause turbidity is plotted as a function of the percentage of B, a calibration curve is obtained, Fig. 2(b), in which each point corresponds to the titration line with the corresponding number in Fig. 2(a). A solution of unknown composition can be titrated, and its composition determined directly from the calibration curve.

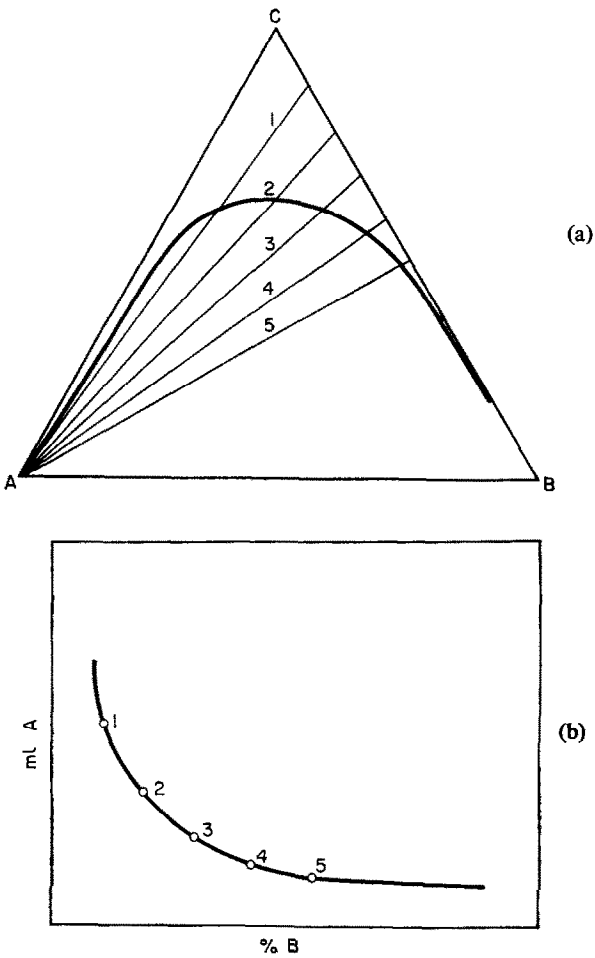


FIG. 2a–b.—The relationship between a three component phase diagram and a calibration curve. Each point on the calibration curve represents the intersection of the corresponding titration line with the solubility curve.

Not only can binary solutions of B and C be determined by titrating with A but homogeneous binary solutions of A and C can be titrated with B to a turbidimetric end-point. In either case, there will be an optimum concentration range of the mixture to be titrated which is dependent on the shape of the phase diagram. Finally, it is possible to determine the ratio of immiscible components of a two phase system, A and B, by titrating with C to the disappearance of turbidity.

Potential sources of error are: (1) variation in temperature caused by ambient fluctuations and heat of mixing, (2) false turbidity caused by air bubbles from too vigorous stirring, and (3) slow attainment of phase equilibrium.

In order to avoid these errors, the reaction flask can be fitted with a constant temperature jacket or the titration can be carried out in a constant temperature bath with a suitable arrangement for observing the phase change through the bath water. Gentle stirring can be maintained and additions of titrant be made very slowly to assure temperature and phase equilibrium throughout the course of

the titration. In addition, an indicator soluble in one component but not in the other can be used to make the appearance of opalescence easier to observe. Large samples can be used to increase the titre.

Taking all of these precautions, very accurate results have been obtained but the method becomes so slow and complicated that its usefulness is questionable.

In the procedure given below, none of these precautions were taken; it was only necessary to run known samples along with the unknown so that the calibration curve was obtained under conditions identical to the titration of unknowns. The technique is so rapid that a calibration curve can be run every day if ambient fluctuations make it necessary to do so.

There are a number of general advantages of phase titrations: (1) In many systems, water is the titrant, eliminating all standardisation, cost and storage problems. (2) There is no indicator, hence no indicator error. (3) The turbidimetric end-point should be well adapted to automatic titrators. (4) Sample size has no effect on the end-point. (5) Ternary mixtures can be analysed by a combination of phase titration and a standard determination of one of the components.[9] (6) There is a vast number of systems to which phase titrations might be applied. One need only think of 10 solvents miscible with water and 10 immiscible with it to have a list of three hundred systems suitable for investigation. (7) A large number of phase diagrams are already in the literature[10,11,12] to serve as a guide for setting up new systems.

EXPERIMENTAL

Reagents

Reagent grade methanol, isopropanol and dioxan were used. Technical grade ethanol, carbon disulphide, carbon tetrachloride and acetone were used. Distilled water was the titrant except as otherwise indicated.

Procedure

The phase diagram, if it is in the literature, may be converted to a rough calibration curve. Guided by the rough curve, five or six binary mixtures were made up and titrated. Their titre was plotted against the volume percentage of the insoluble component. Titrations were carried out using 10 ml of sample in a 25-ml Erlenmeyer flask. Water was added from a 5-ml pump microburette. The solution was stirred vigorously by means of a magnetic stirrer. Splashing was prevented and vaporisation retarded by closing the flask with a one-hole rubber stopper through which the tip of the burette protruded. Water was added rapidly to the appearance of a definite, permanent turbidity. The observance of turbidity was facilitated by strong cross illumination and a black background.

Unknown solutions were determined by comparison with the calibration curve, titrating under identical conditions. If a sample is outside the optimum titration range (a titre of 1 to 10 ml), a known quantity may be diluted with one or the other of its pure components to bring it into the optimum range.

RESULTS AND DISCUSSION

Table I shows the results for a number of binary systems to which phase titrations have been applied. Calibration curves and unknowns were determined on the same day. In each case the calibration curve resembled that shown in Fig. 2(b), the main difference being a displacement away from the x-axis as the water miscible component became less polar. For example, methanol and carbon tetrachloride require less water to cause turbidity than isopropanol and carbon tetrachloride of the same volume composition.

Turbidity, which depends on the difference in refractive index between the two phases, was clearly visible in all cases. The end-point change was rapid in each case except the carbon disulphide-ethanol system which exhibited slow attainment of phase equilibrium and required about a 0·5-min pause between additions of titrant near the end-point. Partial miscibility was observed between carbon disulphide and methyl and ethyl alcohol but this was not encountered between concentrations listed in Table I as the optimum titration concentrations. A considerable heat of mixing effect was observed during the titration of binary solutions containing methanol. Apparently this has not decreased the precision.

Table II shows the results of titration carried out on 5 different days under widely different atmospheric conditions. The results indicate a considerable decrease in reproducibility.

Table III shows, first, the titration of solutions of acetone and water using carbon tetrachloride as the titrant and second, the titration of some heterogeneous mixtures of carbon tetrachloride and water using the principle that binary solutions represented by any of the three sides of a ternary phase diagram can be titrated with the component represented by the opposite apex. The titration of the homogeneous binary systems of acetone and water is in all respects similar to those given in Table I. Titrations of the heterogeneous binary mixtures of carbon tetrachloride and water give a very different

TABLE I. RESULTS FOR THE TITRATION OF 10 HOMOGENEOUS BINARY SYSTEMS WITH WATER. THE END-POINT WAS INDICATED BY THE APPEARANCE OF A DISTINCT PERMANENT TURBIDITY. TITRATIONS AND DETERMINATION OF THE CALIBRATION CURVE WERE CARRIED OUT ON THE SAME DAY

Sample	Optimum range, %	Number of titrations	Standard deviation
CCl_4-methanol	2–30	12	0·16
CCl_4-ethanol	3–50	10	0·31
CCl_4-isopropanol	10–50	15	0·47
CCl_4-dioxane	2–20	8	0·16
CCl_4-acetone	3–25	12	0·26
CS_2-methanol	2–20	17	0·16
CS_2-ethanol	3–20	10	0·12
CS_2-isopropanol	20–40	11	0·14
CS_2-dioxane	3–20	10	0·08
CS_2-acetone	3–25	10	0·11

TABLE II. TITRATIONS OF BINARY SOLUTIONS CARRIED OUT ON 5 DIFFERENT DAYS. ALL SAMPLES WERE COMPARED TO THE SAME CALIBRATION CURVE AND NO CORRECTIONS WERE MADE FOR AMBIENT FLUCTUATIONS

Sample	Optimum range, %	Number of titrations	Standard deviation
CCl_4-isopropanol	20–40	15	1·39
CCl_4-acetone	5–25	15	0·81

TABLE III. TITRATIONS USING TITRANTS OTHER THAN WATER. THE SYSTEM ACETONE-WATER IS HOMOGENEOUS. THE SYSTEM CARBON TETRACHLORIDE-WATER IS HETEROGENEOUS; THE END-POINT IS INDICATED BY THE DISAPPEARANCE OF TURBIDITY

Sample	Titrant	Optimum range, %	Number of titrations	Standard deviation
Acetone–water	CCl_4	4–20	9	0·10
CCl_4–water	Acetone	3–10	9	0·04

calibration curve from Fig. 2(b) because the solubility curve is being approached from the opposite side. Indeed, the more polar titrant, acetone was tried and found to be unsuitable at reasonable proportions of carbon tetrachloride (3%), because the titre was too large; the solubility curve approaches the apex representing acetone too closely.

The titration of heterogeneous mixtures of water and carbon tetrachloride showed an increase in turbidity as the end-point was approached and the emulsion of carbon tetrachloride in the water–acetone system became more stable. Just at the end-point turbidity disappeared and, with very little time lag to establish phase equilibrium, the ternary solution became homogeneous.

Chemistry Department D. W. ROGERS
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Summary—The theoretical basis of phase titrations is discussed, a simple, rapid titration method is described and its errors and advantages are evaluated. Typical calibration curves are shown and related to the corresponding three component phase diagram. Data are included for the analysis of carbon tetrachloride and carbon disulphide

in binary solutions with methanol, ethanol, isopropanol, dioxan and acetone, using water as the titrant. Titrations of heterogeneous systems and titrations using carbon tetrachloride as the titrant are briefly discussed and a few representative results are presented.

Zusammenfassung—Die theoretischen Grundlagen von Phasentitrationen werden diskutiert, eine einfache und rasche Titrationsmethode wird beschrieben und ihre Fehlerquellen und Vorteile werden bewertet. Typische Eichkurven werden gezeigt und mit den dazugehörigen Phasendiagrammen von Dreikomponentensystemen in Beziehung gebracht. Daten für die Analyse von Tetrachlorkohlenstoff und Kohlenstoffdisulfid in binärer Lösung in Methanol, Äthanol, Isopropanol, Dioxan und Aceton unter Verwendung von Wasser als Titrationsmittel werden mitgeteilt. Die Titration heterogener Systeme und Titrationen mit Tetrachlorkohlenstoff werden kurz diskutiert und einige repräsentative Daten gegeben.

Résumé—Les auteurs discutent la base théorique des titrages de phase, décrivent une méthode de titrage simple et rapide et évaluent ses erreurs et ses avantages. Les courbes d'étalonnage caractéristiques sont données et rapportées au diagramme correspondant à trois composés. Les auteurs donnent les résultats d'analyse du tétrachlorure de carbone et du sulfure de carbone en solutions binaires avec le méthanol, l'éthanol, l'isopropanol, le dioxanne et l'acétone, utilisant l'eau comme agent titrant. Les titrages de systèmes hétérogènes, ainsi que ceux qui utilisent le tétrachlorure de carbone comme agent titrant sont brièvement discutés et quelques résultats caractéristiques sont donnés.

REFERENCES

[1] S. Siggia, *Quantitative Organic Analysis via Functional Groups*. J. Wiley, New York, 2nd ed., 1949. p. 189.
[2] S. Siggia and J. G. Hanna, *Analyt. Chem.*, 1949, **21**, 1087.
[3] C. D. Bogin, *Ind. Eng. Chem.*, 1924, **16**, 380.
[4] S. L. Spiridonova, *Analyt. Chem.* (*U.S.S.R.*), 1949, **4**, 169; *Chem. Abs.*, **44**, 2886.
[5] *Idem, J. Appl. Chem.* (*U.S.S.R.*), 1947, **20**, 635; *Chem. Abs.*, **43**, 6946.
[6] *Idem, ibid.*, 1948, **19**, 966; *Chem. Abs.*, **41**, 5809.
[7] E. R. Caley and A. Habboush, *Analyt. Chem.*, 1961, **33**, 1613.
[8] R. Livingston, *Physico-Chemical Experiments*. Macmillan, New York, 1953. p. 135.
[9] A. Findlay, A. N. Campbell and N. O. Smith, *The Phase Rule and Its Applications*. Dover Publications Inc., New York, 1951. Ch. XIII, XIV.
[10] *Int. Crit. Tables*, Vol. III. p. 410.
[11] J. C. Smith, *Ind. Eng. Chem.*, 1942, **34**, 234.
[12] *Idem, ibid.*, 1949, **41**, 2932.

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LETTERS TO THE EDITOR

Photometric determination of uranium in calcium fluoride with 1-(2-pyridylazo)-2-naphthol (PAN) using 1,2-diaminocyclohexanetetra-acetic acid as masking agent

SIR:

CALCIUM fluoride doped with small amounts of uranium^{III} is one of the important optical masers.*[1] A sensitive and accurate method of determining its uranium content is needed. Cheng and Bray[2] reported that small amounts of alkaline earth metals do not give any colour reaction with PAN. It was found, however, that large amounts (for instance, 1 mmole) of alkaline earth metals (also manganese^{II}) give colour reactions with PAN at pH above 9. For the same quantity of the metal, the colour intensities of the complexes follow the order: Mn > Ca > Mg > Ba > Sr. Although addition of EDTA eliminates the interference of calcium, its presence affects slightly the formation of coloured uranium-PAN complex unless its quantity added can be carefully controlled.[3] It was found that 1,2-diaminocyclohexanetetra-acetic acid (DCTA) not only effectively masks the PAN complexes of the interfering metals (including the alkaline earth metals), but also that the presence of its free form does not affect the colour development of the uranium-PAN complex at pH 10. In general, the DCTA complexes are more stable than EDTA complexes. Here it seems that the stability of the uranium complexes is an exception, in that the uranium^{VI}-EDTA complex is more stable than the uranium^{VI}-DCTA complex. At present one cannot compare their stability directly, because their stability constants are not available in the literature. It was also found that DCTA can be successfully used as a masking agent in the determination of uranium with 4-(2-pyridylazo)-resorcinol (PAR),[4] or 1,3-diphenyl-1,3-propanedione,[5] where large amounts of calcium and EDTA also interfere.

The red PAN complexes of alkaline earth metals are presumed to be co-ordinated with molecular water, since they are not extractable by non-polar solvents such as benzene, chloroform, carbon tetrachloride, *etc.*; however, they are extractable by higher alcohols. Large amounts of calcium do not give high results in the determination of uranium because the calcium-PAN complex is not extractable by dichlorobenzene; on the contrary they give low results because of their competition with uranium for PAN. The maximum colour development for the uranium-PAN complex requires at least 5 min of standing.

Calcium fluoride is not decomposed by hydrochloric acid, nitric acid, sulphuric acid, or *aqua regia*. It was found that fuming perchloric acid dissolves it readily.

Procedure: To a finely-ground calcium fluoride sample (approximately 0·2 g) in a 100-ml beaker add 2 ml of 60% perchloric acid, and heat on a hot plate until it is fumed to approximately 1 ml. Cool, transfer to a 100-ml volumetric flask, and make to the mark with water. Take a suitable aliquot (containing not more than 100 μg of uranium) into a small beaker, add a slight excess of DCTA, a few ml of NH_4OH-NH_4Cl pH 10 buffer solution, 1 drop of 2% KCN solution, and 2 ml of 0·1% PAN solution in methanol. Dilute to approximately 20 ml with water, and adjust the pH to 10·0 $\pm$ 0·1 with NH_4OH or HCl, if necessary. Transfer to a 60-ml separatory funnel and let stand for 10–15 min or longer. Add exactly 10 ml of *o*-dichlorobenzene, and shake vigorously for 30–60 sec. Filter the extract through glass wool. Measure the absorbance at 570 mμ against a reagent blank. Assess concentration of uranium from a calibration curve, which has been prepared from known amounts of uranium.

By using the above procedure, excellent results were obtained for synthetic solutions containing 10–100 μg of uranium and 0·1 g of calcium fluoride.

K. L. CHENG

RCA Laboratories,
Princeton, N.J., U.S.A.
1 *April* 1962

REFERENCES

[1] G. C. Dacey, *Science*, 1962, **135**, 71.
[2] K. L. Cheng and R. H. Bray, *Analyt. Chem.*, 1955, **27**, 782.
[3] K. L. Cheng, *ibid.*, 1958, **30**, 1027.
[4] A. I. Busev and V. M. Ivanov, *Vestnik Moskov. Univ., Ser. Khim.*, 1960, No. 3, 52.
[5] R. Přibil and M. Jelinek, *Chem. Listy*, 1953, **47**, 1326.

* *Maser* is an acronym for *m*icrowave *a*mplification by the *s*timulated *e*mission of *r*adiation. An optical maser (also called "laser") is a device for light waves amplification and control to provide a beam which is highly directional, coherent, intense, and nearly monochromatic.

Source of error in arsenic determinations

SIR:

I WONDER whether a source of serious analytical errors which I recently had occasion to encounter, is generally known. If not, it might be of interest to bring it to the attention of your readers. I have not found it clearly mentioned in the literature at my disposal.

When trying to test certain materials for traces of arsenic, the results were positive to a quite improbable degree and also, not reproducible.

The technique used consisted in heating the material in Kjeldahl flasks (adding a few glass balls to prevent bumping) with nitric and sulphuric acids (all of AsT grade) and submitting the residue, after the expulsion of nitrate and chloride, to a modified Gutzeit test with polarographic finish.[1] Many "blanks" on the reagents were negative. Known amounts of arsenic standard solution added to "blanks" were duly recovered, but not only were the results on the material under test improbably high and erratic—also attempts at recovering known quantities of arsenic added to this material had equally unsatisfactory results.

The material under test contained a substantial quantity of fluorides and so, after many frustrating experiments, the suspicion arose that their presence, together with the nitric and sulphuric acids, would lead to attack on the glass and liberation of arsenic should the glass contain arsenic.

This was confirmed by the following experiments.

AnalaR sodium fluoride, when treated with the acid mixture in large platinum crucibles, was found to be practically free from arsenic, and added arsenic was again satisfactorily recovered within the limitations of the method (*q.v.*). When, however, the same test on the sodium fluoride was repeated (also in platinum vessels) with the addition of glass balls of the same batch which had been added to the Kjeldahl flasks in the actual tests to prevent bumping, several hundred μg of arsenic were readily found, the quantity depending upon the number and size of the glass balls added and the quantity of fluoride present.

Porcelain Raschig rings added to the same quantities of sodium fluoride and acids in large platinum crucibles did not yield any arsenic; and these can serve the same purpose as the glass balls. Carborundum chips extracted with *aqua regia* were also very efficient in preventing bumping and did not yield any arsenic.

The writer wonders how generally it is known among analysts how frequently arsenic is added deliberately to glass, both to soft and special glasses, as an oxidising and refining agent. Of two large chemical encyclopedias, one[2] gives, under the heading "Chemical, general scientific and heat resisting glasses" in the specification of Pyrex glass 0·7% As_2O_3, in that of various "British present day types" 0–0·5% As_2O_3.

The other[3] states that mineral acids can dissolve from the glass the As_2O_3 added to the glass melt for decolorising purposes, and that this has to be taken into consideration in the determination of very small amounts of arsenic. The 2nd edition of the same encyclopedia (Vol. 5, 756) quotes Fresenius (without specified reference) as emphasising the importance of this arsenic content of glass for forensic work. This is not in agreement with the negative "blanks" obtained by the writer with nitric and sulphuric acids only, in absence of fluorides. The possible importance of the presence of fluorides is not mentioned; if they are present, their effect is obviously much greater; and in any case these remarks do not seem to have found general attention.

The writer consulted Messrs. Jobling, the makers of the British Pyrex glass, and they wrote that before 1950, Pyrex brand laboratory glassware contained approximately 0·3% of arsenic as As_2O_3, but that now Pyrex is refined by other means and the arsenic level controlled to be less than 5 ppm. Similar information was also received from Messrs. Wood Bros., who also emphasise that in the soft glasses the addition of As_2O_3 is still fairly common practice, and that one would expect to find up to 0·5% of arsenic in glasses of this type.*

It seems noteworthy, however, that the writer also found arsenic (although in very much smaller quantity than in the presence of glass balls) when treating fluorides in Kjeldahl flasks with nitric and sulphuric acids, using either porcelain Raschig rings or platinum gauze instead of glass balls, although there was hardly a visible attack of the flask, and its loss in weight was only of the order of 0·1–0·2 g. The quantity of arsenic found in the reaction product varied from flask to flask and was of the order of 1 to 10 μg, hence enough to be troublesome in certain cases.

The material under test contains, apart from fluoride, also large amounts of chloride, and thus cannot be treated with nitric acid in platinum vessels; silica vessels did not yield arsenic but were badly attacked, much more than borosilicate glass. Large porcelain crucibles (Royal Worcester) were eventually used, which suffered only slight attack during the analysis and did not yield any arsenic, although they lost their glaze after one or two tests, which did not seem to make them unserviceable.

* The information received from both firms is acknowledged with thanks.

It may be said that this source of error will not often come into play in the practice of arsenic determination. It would, however, operate if one were to test minerals like cryolite or fluorspar or other fluorides for arsenic, but it might even become important in (admittedly rare) forensic cases, *e.g.* a test for arsenic might be called for if for some reason the suspicion of arsenical poisoning arose in a case which in fact was one of fluoride poisoning. If the wrong type of glass (be it glass balls or vessels) were used, ordinary "reagent blanks" would *not* offer any protection against the error described, as normally no fluoride would be added to a control.

Greenland cryolite and fluorspar also came within the scope of the writer's test series, and there these spurious findings of arsenic seemed to fall in line with a remark in the literature (which in this case acted as a kind of "red herring") that arsenopyrite is one of the minerals found associated in small amounts with the cryolite. In fact, however, the specimen of cryolite tested was practically free from arsenic.

These experiments were carried out in the laboratory of International Alloys Ltd., Haydon Hill, Aylesbury, Bucks., England, and the permission of the Management to publish them is acknowledged with thanks.

I am, Sir,
Yours faithfully,
(Dr.) W. STROSS
Chief Chemist

International Alloys Ltd
Haydon Hill,
Aylesbury, Bucks., England
28 *June* 1962

REFERENCES

[1] B. Cristau, *Bull. Soc. chim. France*, 1958, 717; L. Vignoli, B. Cristau and F. Gouezo, *Chim. analyt.*, 1961, 43, 439.
[2] Thorpe, *Dictionary of Applied Chemistry*. 4th Ed., 1941, Vol. V, 557.
[3] Ullmann, *Enzyklopaedie der Technischen Chemie*. Urban und Schwarzenberg, 3rd Ed., 1957, Vol. VIII, 146.
[4] W. E. Ford, *Dana's Manual of Mineralogy*, J. Wiley and Sons, New York: Chapman and Hall, London, 14th Ed. 1928, 185.

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BOOK REVIEWS

Dosages Colorimétriques des Éléments Minéraux. G. CHARLOT. Masson et Cie, Paris, 1961. 2nd Edition. Pp. 379.

THERE are several comprehensive works on colorimetric methods of analysis, and serviceable as such books may be, they are frequently top-heavy in some respects, with a mass of somewhat superfluous detail and out-of-date material. There is most certainly room for a new book on this topic which is cut on cleaner lines, and which has a newer and less cumbered approach. No one can disagree that the modern trend has been away from the classical techniques of gravimetric and titrimetric analysis towards something which requires less manipulation by an operator. In recent years many of the more exotic physical methods of analysis have held sway, but some of these are, in perspective, now realised to be rather expensive and troublesome in the demands they make on the operator's time and knowledge of electronics and physics as well as of chemistry. The advent of automatic methods of analysis has considerably redressed the balance, with the results that simpler and more rugged methods are again more widely used. Absorptiometry, or spectrophotometry, is such a technique. Based on simple pH adjustment, standard reagent addition and simple one-parameter measurement, it can be automated readily to determine a wide variety of metals, non-metals, organic compounds, *etc.* on a single automatic instrument. As a result, there is little doubt that the technique will largely replace gravimetry and titrimetry as the standard routine method of analysis. The range of modern spectrophotometers has removed the difficulty of dealing with large amounts of materials since these can now be resolved satisfactorily by a differential technique with the sensitive detecting devices of modern instruments.

The present book has a comprehensive outlook, yet it maintains a reasonable size by virtue of its arrangement and planning. Part I, sub-titled *Généralités*, deals with the fundamental laws of light absorption and methods of measurement, with technique and attainable precision, and with the choice of conditions for applying a spectrophotometric method. It also discusses less-frequently used techniques such as fluorimetry, turbidimetry, nephelometry and photometric titration. Extensive coverage is given to modern separation/concentration methods such as solvent extraction, chromatography, ion-exchange, electrodeposition, adsorption on carriers and distillation.

Part II details the determination of the elements from aluminium through to zirconium, and includes some non-metals in their more common ionic forms, *e.g.* sulphur, nitrogen, oxygen, phosphorus, fluorine, silicon, *etc.* With commendable economy it also covers very fully less common elements such as rhenium, iridium, osmium, germanium, *etc.* Each element is treated in brief monograph form, with an account of the appropriate separation methods noted above; and the principles and working details of the experimental procedure for the more important methods are clearly outlined. Admirable coverage is given to the influence of foreign ions and the elimination of interferences. In each case a fairly extensive bibliography is appended, and "off-beat" methods are by no means ignored.

Taken all over, this book is well balanced, up-to-date, delightfully critical, well informed in its approach and altogether the best book on spectrophotometry I have so far met.

T. S. WEST

Anodic Oxide Films. L. YOUNG. Academic Press Inc., New York: Academic Press Ltd., London, 1961. pp. 377. 70s.

DR. Lawrence Young has been an active researcher in the field of anodic oxidation for the last decade. On seeing a pre-publication notice of this book the reviewer anticipated that it would be comprehensive, argumentative and stimulating. These anticipations have been fully realised.

It will be undoubtedly of great value to those active in this field of research, as well as collecting much of the recent data which is invaluable for persons who either require up-to-date information, but are not themselves active in research, or are engaged on allied topics (*e.g.* solid state chemistry, metallic corrosion).

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The author has divided the book into two main sections: first a general section dealing with fundamental principles and experimental techniques used in anodic oxidation studies, and then a more specific section occupying more than half the book. This latter section deals in detail with a large number of metals and semiconductors in turn, probably covering all the systems worthy of discussion. The author has attempted to follow critically the development of thought in each case and the reviewer found this particularly stimulating.

There is a short appendix which is meant to give the non-specialist an insight into the subject. Each chapter has copious up-to-date references to original papers.

M. W. ROBERTS

Photometric Titrations. J. B. HEADRIDGE. Pergamon Press, London, 1961. pp. x + 131. 45s.

THIS monograph on photometric titration is the first of its kind, yet it approaches the topic with a sureness of purpose and treatment which is characteristic of an experienced author writing on a subject already well documented and one where pitfalls and inadequacy of treatment are already well known.

The text begins with the historical background of the method, then reviews various types of titration, sources of error peculiar to this technique and theoretical curves with and without added indicator substances. This introductory section ends with a useful account of end-point indices. The ensuing section reviews apparatus, and the remainder of the text details methods for acid-base, oxidation-reduction, complexometric and precipitation titrations. The last two chapters are concerned with coulometric titrations which make use of photometric end-points and with miscellaneous methods, *e.g.* the titration of water in glacial acetic acid, micelle concentration in soap solutions, photonometric titrations, *etc.*

This little book gives a really first-class account of this relatively new technique, and does not suffer from the all too frequent over-enthusiasm and over-emphasis which is prevalent in so many monographs on new techniques of analysis. Thus, on the very first page the author warns that there is little point in carrying out a photometric titration if a satisfactory visual indicator is already available. While the reviewer is not convinced of the logical necessity of bolstering up a troublesome titration by having resource to photometric detection of the end-point when frequently a non-titrimetric method might be applied, he fully recognises that this is a matter of policy to be decided by the individual analyst. For those who prefer to apply a titrimetric method under such circumstances, Dr. Headridge has performed an invaluable service. The topic is presented very clearly in an attractive manner and with full working details for all the more important procedures.

T. S. WEST

Dissociation Constants of Organic Acids in Aqueous Solution. Compiled by G. KORTÜM, W. VOGEL and K. ANDRUSSOW, for the International Union of Pure and Applied Chemistry, Section of Analytical Chemistry, Commission on Electrochemical Data. Butterworths, London, 1961. pp. xxii + 357, 50s.

THIS is a very useful compilation of data. The tables are preceded by an excellent critical survey of methods of measurement (printed in both English and German) which explains the theoretical basis of the available methods and assesses their relative accuracy. The tables themselves are extensive, listing dissociation constants for 1056 organic acids, together with an indication of the method of determination and the probable reliability of the results for each acid. There are over 400 references to the literature. The tables are clearly laid out and the volume is well printed and produced.

J. E. B. RANDLES

Quimica Analytica Cualitativa. J. RAMIREZ-MUNOZ and G. SALCEDO-ESCOBAR. Ediciones UIS, Universidad Industrial de Santander, Bucaramanga, Colombia, 1961. pp. 347.

A MORE appropriate title for the book would be *Laboratory Manual for Qualitative Analysis.* This would indicate that the impressive 347 pages actually boil down to about 100 filled with text, the rest consisting of sheets with some lines and check squares to be filled in by the student in order to report his analysis. The 100 pages, containing instructions on how to handle laboratory ware and schedules for analysis are, however, extremely good. The book is based on the conventional hydrogen sulphide procedure

The author has divided the book into two main sections: first a general section dealing with fundamental principles and experimental techniques used in anodic oxidation studies, and then a more specific section occupying more than half the book. This latter section deals in detail with a large number of metals and semiconductors in turn, probably covering all the systems worthy of discussion. The author has attempted to follow critically the development of thought in each case and the reviewer found this particularly stimulating.

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T. S. WEST

Dissociation Constants of Organic Acids in Aqueous Solution. Compiled by G. KORTÜM, W. VOGEL and K. ANDRUSSOW, for the International Union of Pure and Applied Chemistry, Section of Analytical Chemistry, Commission on Electrochemical Data. Butterworths, London, 1961. pp. xxii + 357, 50s.

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J. E. B. RANDLES

Quimica Analytica Cualitativa. J. RAMIREZ-MUNOZ and G. SALCEDO-ESCOBAR. Ediciones UIS, Universidad Industrial de Santander, Bucaramanga, Colombia, 1961. pp. 347.

A MORE appropriate title for the book would be *Laboratory Manual for Qualitative Analysis.* This would indicate that the impressive 347 pages actually boil down to about 100 filled with text, the rest consisting of sheets with some lines and check squares to be filled in by the student in order to report his analysis. The 100 pages, containing instructions on how to handle laboratory ware and schedules for analysis are, however, extremely good. The book is based on the conventional hydrogen sulphide procedure

The author has divided the book into two main sections: first a general section dealing with fundamental principles and experimental techniques used in anodic oxidation studies, and then a more specific section occupying more than half the book. This latter section deals in detail with a large number of metals and semiconductors in turn, probably covering all the systems worthy of discussion. The author has attempted to follow critically the development of thought in each case and the reviewer found this particularly stimulating.

There is a short appendix which is meant to give the non-specialist an insight into the subject. Each chapter has copious up-to-date references to original papers.

M. W. ROBERTS

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H. G. HEAL

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R. G. H. B. BODDY

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any of the impurities there listed. In the last decade, however, a quiet revolution has been taking place in the standards of purity of commercial chemicals, and many elements and compounds can now be obtained with a total impurity content of only a few parts per million. The demand for these, arising from industry, universities and government departments, has been met by means of new techniques of purification (zone melting, ion exchange, *etc.*), with the help of new and extremely refined methods of purity control (such as vapour phase chromatography).

This report describes what happened when attempts were made to prepare very pure metals by the decomposition of organometallic compounds. These were thought to offer some promise because their volatility allows them to be purified by physical methods not suitable for most of the inorganic compounds of the metals. The standard of purity aimed at was a content of less than 0·001 ppm of any impurity. Full success was achieved only with mercury, which was formed in a state of absolute spectroscopic purity by the photolysis of diethyl mercury. The pyrolysis of rhenium and nickel carbonyls gave metal samples of good purity, but not nearly approaching the 0·001-ppm standard. Impure magnesium was obtained by the electrolysis of ethyl magnesium hydride. No results of any value were obtained with organocalcium and organogallium compounds. The whole report is of an exploratory character; none of the investigations described could be regarded as exhaustive or final; and much of its value lies in the guidance it will give to future experimenters.

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Statistical Mechanics. NORMAN DAVIDSON. McGraw-Hill Publishing Co. Ltd., London: McGraw-Hill Book Company, Inc., New York, 1962. pp. ix + 540. £5.12.6.

STATISTICAL mechanics are concerned with the derivation of the macroscopic properties of materials, such as pressure, heat capacity, entropy, magnetic susceptibility, *etc.* from a knowledge of the quantum state accessible to the atoms or molecules making up the material. Often the calculation of the macroscopic property by the methods of statistical mechanics is easier than direct measurements: in all cases statistical mechanics provide the theoretical link between the two types of knowledge and thus indicates what are the important atomic or molecular factors that determine the macroscopic property. Applications of methods of statistical mechanics to problems in analytical chemistry are as yet few: one such is the application to the equilibria of isotope fractionation reactions.

By their nature, statistical mechanics are mathematical and depend upon the logically prior subjects of classical mechanics and quantum mechanics. At the same time the subject has many and diverse applications in physics and chemistry. To write a successful book on statistical mechanics for chemists is, therefore, not easy. Professor Davidson, in his book, presents the fundamentals and main applications of the subject lucidly and thoroughly. The book will be valuable to the chemist who wishes to understand the mathematical and theoretical basis of the subject and who is prepared to read the text carefully and to work through at least those of the problems which are interspersed in the main text. Mathematics of approximately university subsidiary standard is required.

Professor Davidson devotes quite a large part of the book to concise accounts of subjects which are either logically prior to statistical mechanics, such as classical mechanics and quantum mechanics, or subjects like spectroscopy and the activity coefficients of ions in solution, of which a knowledge is needed for the application of statistical mechanics in the system considered. Generally these accounts are good, though the reviewer feels that many topics are discussed so concisely that the reader who is not previously acquainted with (to take a few examples) Lagrange's and Hamilton's equations of motion, quantum mechanical operators or the calculation of the vibration frequencies of polyatomic molecules, will find the going difficult.

In a few cases the presentation could be improved. The reader might well spend considerable time puzzling over equation (3-6d) without reading the further half page necessary to discover that the rule he or she had been trying to apply, given on the previous page, did not hold in this case. Omission of ". . ." made several equations (from a pedantic viewpoint) not true.

In places it seemed to this reviewer that the treatment tended to be unnecessarily austere, and that the mathematical bare bones were not sufficiently covered with chemical fact: perhaps an example of this tendency is the single seventeen-year-old reference given on p. 194 to (presumably) data on characteristic vibration frequencies.

These are, however, minor criticisms of a well-written, useful and thorough book: the fact that it is written as a standard classroom textbook for graduate students in America is food for thought for those who teach students elsewhere.

A. D. E. PULLIN

any of the impurities there listed. In the last decade, however, a quiet revolution has been taking place in the standards of purity of commercial chemicals, and many elements and compounds can now be obtained with a total impurity content of only a few parts per million. The demand for these, arising from industry, universities and government departments, has been met by means of new techniques of purification (zone melting, ion exchange, *etc.*), with the help of new and extremely refined methods of purity control (such as vapour phase chromatography).

This report describes what happened when attempts were made to prepare very pure metals by the decomposition of organometallic compounds. These were thought to offer some promise because their volatility allows them to be purified by physical methods not suitable for most of the inorganic compounds of the metals. The standard of purity aimed at was a content of less than 0·001 ppm of any impurity. Full success was achieved only with mercury, which was formed in a state of absolute spectroscopic purity by the photolysis of diethyl mercury. The pyrolysis of rhenium and nickel carbonyls gave metal samples of good purity, but not nearly approaching the 0·001-ppm standard. Impure magnesium was obtained by the electrolysis of ethyl magnesium hydride. No results of any value were obtained with organocalcium and organogallium compounds. The whole report is of an exploratory character; none of the investigations described could be regarded as exhaustive or final; and much of its value lies in the guidance it will give to future experimenters.

H. G. HEAL

Statistical Mechanics. NORMAN DAVIDSON. McGraw-Hill Publishing Co. Ltd., London: McGraw-Hill Book Company, Inc., New York, 1962. pp. ix + 540. £5.12.6.

STATISTICAL mechanics are concerned with the derivation of the macroscopic properties of materials, such as pressure, heat capacity, entropy, magnetic susceptibility, *etc.* from a knowledge of the quantum state accessible to the atoms or molecules making up the material. Often the calculation of the macroscopic property by the methods of statistical mechanics is easier than direct measurements: in all cases statistical mechanics provide the theoretical link between the two types of knowledge and thus indicates what are the important atomic or molecular factors that determine the macroscopic property. Applications of methods of statistical mechanics to problems in analytical chemistry are as yet few: one such is the application to the equilibria of isotope fractionation reactions.

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A. D. E. PULLIN

Bevezetés a komplex vegyületek kémiájába (Introduction to the Chemistry of Complex Compounds). A. A. GRINBERG. Akadémiai Kiadó, Budapest, 1958. pp. 408. 95 Hungarian forints. In Hungarian.

THIS book is a translation of the second Russian edition published in 1951. This date itself determines that the book cannot account for the enormous progress of co-ordination chemistry during the last decade. Apart from this disadvantage the book is a valuable contribution to the literature of complex chemistry, since it treats thoroughly the results of "classical" complex chemistry. The author is a distinguished member of the Soviet school of complex chemistry and so the book gives an authentic review of the subject, especially of the results achieved between the two World Wars.

The book consists of an Introduction and eleven Chapters. Chapter 1 gives a survey of some simple types of co-ordination compound. Chapter 2 deals with Werner's theory and also touches on its predecessors. Chapter 3 deals with the stereochemical consequences of the octahedral configuration, while Chapter 4 continues the review of the complexes of co-ordination number six. Chapter 5 treats the complexes of co-ordination number four, especially the complexes of platinum. Chapter 6 summarises the different types of isomerism, while Chapter 7 deals with the nature of chemical bonding in complexes. The complete lack of a review of modern theories is regrettable. Chapter 8, which treats the mutual effects of co-ordinated groups, especially the problems of *trans* effect, is particularly interesting. Chapter 9 gives a too short account of the solution chemistry of complexes, while Chapter 10 touches on some special types of co-ordination compound. In the last chapter one finds an interesting attempt to relate the complex forming ability of elements with their position in the periodic system.

As can be seen from the above list, the contents of the book comprise almost the whole field of complex chemistry. In some respects, especially in the stereochemistry of complex compounds, it is much more than an introduction for a beginner. Nevertheless, as a whole, it does not give a satisfactory picture even for a novice because of the lack of the newer achievements which have not only widened enormously our knowledge, but have also modified our view of inorganic chemistry.

The reviewer understands that the author is working on a new revised edition. Knowing the valuable features of the present book this new version is eagerly awaited.

The translation is in general fairly good, the text is very readable, but some superficialities in the double transcription of the non-Russian names has resulted in puzzles for the reader.

M. T. BECK

Talanta, 1962, Vol. 9, pp. 749 to 753. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

(Material for this section should be sent directly to the Associate Editor)

ARGENTINA

Sunday–Saturday 16–22 *September* 1962: **Eighth Latin-American Congress of Chemistry.** Buenos Aires (see *Talanta*, 1962, **9**, 184).

CANADA

Monday–Wednesday 17–19 *September* 1962: **Ninth Ottawa Symposium on Applied Spectroscopy:** *Canadian Association for Applied Spectroscopy.* Ottawa (see *Talanta*, 1962, **9**, 399).

FRANCE

Lundi–Vendredi 1–5 *Octobre* 1962: **XIII^{èmes} Journées Pharmaceutiques Françaises:** organisées par *la Société de Technique Pharmaceutique.* Paris.

Sunday 26 *May–Saturday* 1 *June* 1963: **Sixth International Mineral Processing Congress:** *Société de l'Industrie Minérale.* Cannes (see also *Talanta*, 1961, **8**, 764).

The provisional programme is now available from the Secrétariat Général du 6^{e} Congrès International de la Préparation des Minerais, 28, Rue Arthur-Rozier, Paris XIX^{e}, France.

JAPAN

Monday–Saturday 10–15 *September* 1962: **International Symposium on Molecular Structure and Spectroscopy:** *I.U.P.A.C.* and *Science Council of Japan.* Tokyo (see *Talanta*, 1962, **9**, 401).

UNITED KINGDOM

Sunday–Saturday 9–15 *September* 1962: **Fifth Triennial Summer School in Analytical Chemistry:** *Royal Institute of Chemistry* with the participation of *Society for Analytical Chemistry.* Manchester College of Science and Technology (see *Talanta*, 1961, **8**, 913).

Monday–Wednesday 17–19 *September* 1962: General Discussion on **High Resolution Nuclear Magnetic Resonance:** *Faraday Society.* University of Oxford, Laboratory of Physiology, South Parks Road, Oxford.

The papers will be presented and discussed under the following headings:

1. Nuclear Magnetic Resonance in Diamagnetic Materials.
2. Nuclear Magnetic Resonance in Paramagnetic Materials.
3. Applications to the Determination of Molecular Structure.
4. Applications to the Study of Kinetic Processes.

Further details may be obtained from The Secretary, The Faraday Society, 6 Gray's Inn Square, London, W.C.1.

Tuesday–Friday 18–21 *September* 1962: **First International Congress of Food Science and Technology.** Imperial College of Science and Technology, South Kensington, London, S.W.7 (see *Talanta*, 1962, **9**, 403).

Friday–Saturday 21–22 *September* 1962: **Modern Trends in Small-Scale Inorganic Analysis:** *Society for Analytical Chemistry, Microchemistry Group and Royal Institute of Chemistry, Dublin and District Section.* Dublin.

The **National Lending Library for Science and Technology** announces the following changes of procedure:

1. All loan requests which hitherto would have been sent to the Science Museum Library should now be sent to the NLL at Boston Spa, Yorkshire, addressed to the Loans Department.
2. Requests for borrowing facilities or for the supply of loan forms should be sent to the NLL at Boston Spa, addressed to the Director.

To facilitate the smooth development of the NLL's loan service:—

(a) requests for the supply of photocopying forms and

(b) individual photocopy requests

should continue to be sent to the Science Museum Library, South Kensington, London, S.W.7, except where it is known that the publications are not likely to be available there.

The following information is intended for those wishing to obtain *translations of foreign scientific literature* from **Aslib** or the **National Lending Library for Science and Technology**. The services provided are available to all individuals and organisations in the United Kingdom, whether or not they are members of Aslib.

Aslib (3, Belgrave Square, London, S.W.1) maintains the U.K. copy of the British Commonwealth Index of Scientific Translations. This is a location index for translations, mostly unpublished, made in the principal countries of the Commonwealth *from all languages* into English. It also includes details of translations collected since January 1959 under the American O.T.S./S.L.A. scheme and now listed in *Technical Translations*. The U.K. copy is intended to be the central checkpoint for the U.K. at which persons or organisations can ascertain whether a given article has been translated and, if so, from which, and conditions on which, it can be borrowed.

The National Lending Library for Science and Technology (Boston Spa, Yorkshire) collects and lends translations *from the Russian*. Details of these translations are incorporated in the Aslib index, with the exception of a few made before 1959.

British Standards Institution announces the following **New British Standards:**

B.S. 1428: *Microchemical apparatus: Group E general accessory apparatus: Part E* 4: 1962: *Crucible Holder, microburner, spatulas and forceps.*

This specifies the following items of apparatus for use in microchemical analysis:

(i) Crucible holder suitable for use in the ignition of crucibles of top diameter up to about 60 mm including all types of crucibles specified in B.S. 1428 Part E 1.
(ii) Microburner jet for use with coal gas, giving a non-luminous flame up to about 5 cm in height.
(iii) Three types of spatula; heavy stainless steel, light stainless steel and light platinum-tipped with hollow stainless steel shaft.
(iv) Reverse action and normal action forceps.

The specification also recommends a suitable micro burner and includes fully dimensioned drawings (Price 5s.).

B.S. 3473: 1962: *Methods for testing the chemical resistance of glass used in the production of laboratory glassware.* This describes methods for determining the resistance of types of glass used in the production of laboratory glassware towards attack by

(i) A boiling aqueous solution of mixed alkali.
(ii) Water at 100°.
(iii) Water at 121° in an autoclave.

The test procedures are based on two German standards and one United States standard (Price 5s.).

B.S. 3517: 1962: *Methods for thermal shock tests on laboratory glassware.* This describes three methods for determining the resistance to thermal shock of the types of glass used in the production of laboratory glassware, *i.e.* for testing whole articles at temperature differences less than 100°, for testing whole articles at temperature differences of 100° or more and for testing the rims of articles (Price 3s.).

B.S. 3513: 1962: *Gamma-radiography sealed sources.* This specifies general constructional requirements, tolerances on source activity and radiation output, and dimensions, both of the radioactive material and the outer capsule for gamma-ray sources of activity up to *ca.* 100 curies for cobalt-60 or 300 curies for caesium-137 or iridium-192. Test requirements with regard to freedom from surface radioactive contamination and leak freedom are given, with details of the test methods, and requirements are also laid down concerning the marking of the sources and the provision of certain certificates. The specification replaces B.S. 2783 which specified source capsules only (Price 5s.).

The following *Revised British Standards* are also announced:

B.S. 700: 1962: *Graduated pipettes.* This specifies three types of graduated pipette: Type 1 calibrated for delivery from zero line to graduation line, Type 2 calibrated for delivery down to jet, Type 3 calibrated for content, and 1-, 2-, 5-, 10- and 25-ml sizes for each type of pipette. It gives full dimensions, but lists only the essential ones as mandatory, the remainder being given for the guidance of manufacturers. It includes standard methods for the determination of capacity and delivery time, and tolerances for both, as well as requirements for material, construction, graduation and marking (Price 5s.).

B.S. 1428: *Microchemical apparatus: Group C apparatus for determination of organic groups: Part C* 1: 1962: *Alkoxyl and alkylimino group determination apparatus.* This specifies components for use in the micro determination of alkoxyl groups by the Zeisel method and of alkylimino groups by the Friedrich method. It describes Zeisel apparatus with ground glass joints and Friedrich apparatus and also a glass weighing spoon for use with the former. It includes fully dimensioned drawings for all components (Price 5s.).

The following *Amendment Slips* are also announced:

B.S. 769: 1961: *Chemical analysis of butter. Amendment No.* 1: *PD* 4556.
B.S. 812: 1960: *Methods for sampling and testing mineral aggregates, sands and fillers. Amendment No.* 1: *PD* 4563.
B.S. 1647: 1961: *pH Scale. Amendment No.* 1: *YD* 4565.

UNITED STATES OF AMERICA

Wednesday–Friday 5–7 *September* 1962: **Symposium on Measurement of Thermal Radiation Properties of Solids:** *Aeronautical Systems Division, U.S.A.F., National Bureau of Standards and National Aeronautical and Space Administration.* Biltmore Hotel, Dayton, Ohio.

Sunday–Friday 9–14 *September* 1962: **142nd National Meeting of American Chemical Society.** Atlantic City, N.J.

Sunday–Thursday 16–20 *September* 1962: **Second Annual Conference on Pharmaceutical Analysis.** King's Gateway, Land O'Lakes, Wisconsin (see *Talanta*, 1962, **9**, 406).

Wednesday–Friday 26–28 *September* 1962: **Practice of Gas Chromatography:** *A.S.T.M. Committee E-19* and *Michigan State University.* Michigan State University.

Wednesday–Friday 14–16 *November* 1962: **1962 Eastern Analytical Symposium and Instrument Exhibit:** *Analytical Chemistry Groups of American Chemical Society* of New York and North Jersey Sections, and New York, Delaware Valley, New England and Baltimore-Washington Sections of Society for Applied Spectroscopy, and Metropolitan Microchemical Society. Statler Hilton Hotel, New York.

The meeting will consist of a series of 3-hr symposia of invited papers of extended length by experts in a number of fields of interest to analysts. The emphasis will be on recent developments in these specialities. The exhibition will consist of 85 manufacturers of scientific apparatus and supplies.

The detailed programme of symposia is as follows:

Wednesday 14 *November:* 9.00 a.m.

Thermal Analysis

Thermometric Titrations.	J. JORDAN
Cryoscopic Evaluation of Purity.	R. J. BEST
Thermogravimetry and DTA.	S. GORDON

Gas Chromatography in Medical Research

Analyses of Urinary Steroids by Gas Chromatography.	R. ROSENFELD
Use of Gas Chromatography in the Study of Hypocholesterolemic Agents.	W. HOLMES
A Study of the Fatty Acids and Aldehydes of Human Platelet Phosphatides by Gas Chromatography.	A. MARCUS

Wednesday 14 *November:* 2.00 p.m.

Preparative Gas Chromatography

Preparative Gas Chromatography.	H. FELTON
Preparative Gas Chromatography in Academic Research.	J. AMY
New Approaches to Preparative Gas Chromatography.	H. SZYSMANSKI
Panel Discussion of Gas Chromatography.	

Analytical Applications of NMR

The Realm of NMR—High Resolution, Broad Line and Relaxation Phenomena.	L. N. MULAY
NMR Relaxations in Polymer Melts and Solutions.	D. MCCALL
NMR Applied to Polymer Research.	J. A. SAUER
Quantitative Aspects of NMR.	H. FOSTER

Thermal Analysis of High Polymers

DTA of High Polymers.	J. R. KNOX
DTA Instrumentation for High Polymer Studies.	J. CHIU
Thermogravimetry in Polymer Research.	C. D. DOYLE
Effluent Analyses in Thermal Studies.	P. A. GARN

Advances in Instrumentation Clinic

Analytical Instrumentation in the Medical Sciences—S. NATELSON

Thursday 15 *November:* 9.00 a.m.

New Developments in Excitation Sources

Excitation of Various Elements by Radio Frequency Excitation: Potential Analytical Applications.	R. MAVRODINEANU and R. C. HUGHES
Optical Microemission Stimulated by a Ruby Laser.	F. BRECH
Plasma Jets and Gas-Stabilised Arc Sources.	M. MARGOSHES

Quantitative Micro Analysis

Use of X-rays in Quantitative Clinical Chemistry.	S. NATELSON
Determination of Fluorine and Oxygen by Neutron Activation.	R. STEELE
Quantitation in Inorganic Microchemistry.	K. CHENG

X-rays in Polymer Analysis

Use of Pole Figure Analysis in the Study of Polymers.	P. H. LINDENMEYER
Studies of Partially Ordered Crystalline Polymers.	H. W. WYCKOFF
Studies of Low Angle X-ray Scattering from Polymers.	W. O. STATTON

Thursday 15 *November:* 2.00 p.m.

Recent Applications of Electron Probe Microanalysis

Geological and Mineralogical Applications of the Microprobe.	I. ADLER
Analytical Procedures in Microprobe Analysis.	T. ZIEBOLD
Metallurgical Applications of the Scanning Beam Microprobe.	R. M. FISHER

Chromatography

Thin Layer Chromatography.	E. WOLLISH
Electrophoresis.	P. PLAISTED
Paper Chromatography.	H. STRAIN

Molecular Weight Measurements

Number Average Molecular Weights Osmometry.	W. R. KRIGBAUM
Ebulliometry.	M. EZRIN
Weight Average Molecular Weights Light Scattering.	D. MCINTYRE
Equilibrium Ultracentrifugation.	D. A. YPHANTIS
Nonequilibrium or Transport Numbers.	W. H. STOCKMAYER
Fractionation.	N. S. SCHNEIDER

Advances in Instrumentation Clinic

Gas Analysis (Gas Chromatography-Absorption Spectroscopy-Mass Spectroscopy)—R. GOHLKE

Friday 16 *November:* 9.00 a.m.

Symposium on Evaluation of Spectrophotometric Performance

Instrumental Parameters in Spectrophotometry.	R. C. HAWES W. KAYE W. SLAVIN

Trace Analysis

Modern Techniques of Trace Element Analysis.	G. H. MORRISON
Activation Analysis with Portable Neutron Generators.	E. L. STEELE
Analysis of Solid State Materials.	S. J. ADLER
Meaning of Trace Metal Analysis to the Biological Sciences.	B. L. VALLEE

Chemical Microscopy

Introduction and General Applications.	F. W. FARWELL
Theory and Principle of Measurement.	P. BARTELS
Specialised Applications including Pleochromism.	M. WILLARD

Friday 16 *November:* 2.00 p.m.

Symposium on Evaluation of Spectrophotometric Performance

Wavelength and Photometric Standards in Infrared Spectrophotometry.	M. K. WILSON
Photometric Standards in Visible and Ultraviolet Spectrophotometry.	J. M. VANDENBELT

Panel Discussion: Speakers from both sessions.

Qualitative Organic Microchemistry

Techniques and Applications in Organic Qualitative Analysis.	N. CHERONIS
Crime and Crystallography.	L. DALCORTIVO
Identification of Unsaturation.	J. SHARESKIN

Advances in Instrumentation Clinic: 2.00 p.m.

Quality Control in Emission Spectroscopy—Automation.	R. J. CARLS
Sample Preparation Techniques in X-ray Spectroscopy.	G. CRUMRINE

Further information may be obtained from P. LUBLIN, General Telephone and Electronics Laboratories Inc., Bayside Laboratories, Bayside 60, N.Y.

In co-operation with National Bureau of Standards, the Atomic Energy Commission has prepared a chemical standard sample of plutonium for use by educational and research institutions in the United States and abroad. Having a purity of 99·97%, the plutonium sample (NBS Standard Sample No. 949) can be utilised as a comparison standard for all plutonium chemical analyses. Each sample consists of about 0·5 g of plutonium metal sealed in a glass ampoule under reduced argon atmosphere.

A new radioactivity standard sample, cobalt-57, and three reissues of previously available standards, zinc-65 and two concentrations of sodium-22, are now being distributed by the Bureau. All are in solution form except the zinc standard, which is prepared as a point source deposited on a mylar film.

The Bureau has recently issued *Standard Materials*, Miscellaneous Publication 241, a catalogue which lists the standard materials—over 600 different standards of metals, ores, ceramics, chemicals and hydrocarbons—available from the Bureau with their prices, shipping weights and directions for ordering. Summarised tables of analyses are also presented to indicate the types of standards of composition presently available. The publication may be obtained for 30 cents from the Superintendent of Documents, U.S. Government Printing Office, Washington 25, D.C.

ERRATA—VOLUME 9

Page 381, line 5: for *stimulate* read *simulate*.

Page 384, the heading on the last column of Table III should refer to the footnote by reading *Corrected*[a].

Page 387, *Introduction, line* 8: this should read *complex fluoride ions. All of the fluoride, both free and in the form of tantalum complex, complexes with boron.*

Page 449, *Preliminary Communication by F. Vydra and V. Marková: Received* 13 *February* 1962. *Accepted* 22 *February* 1962.

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Talanta, 1962, Vol. 9, p. 754. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Detection and quantitative estimation of some polynuclear hydrocarbons by electron spin resonance: B. D. FLOCKHART and R. C. PINK. (28 *May* 1962).

Amperometrische Bestimmung der Metalle unter der Anwendung von Thioacetamid—IV: Untersuchungen über Tl_2S-Bildungsgeschwindigkeit in ammoniakalischen Tl^+-Ionenlösungen mittels Thioacetamid (TAA): MARIA PRYSZCZEWSKA. (30 *May* 1962).

Spectrophotometric determination of iron in high-purity niobium, tantalum, molybdenum and tungsten metals: ELSIE M. PENNER and W. R. INMAN. (1 *June* 1962).

Studies of the absorptiometric determination of soluble phosphorus in textiles: J. T. MCALOREN and G. F. REYNOLDS. (1 *June* 1962).

Photometric determination of aluminium with xylenol orange: EVA PAVLÍKOVÁ and JOSEF JANKOVSKÝ. (1 *June* 1962).

Contribution to the basic problems of complexometry—X: Determination of nickel and cobalt in the presence of iron, copper and some other metals: RUDOLF PŘIBIL and VLADIMÍR VESELÝ. (11 *June* 1962).

Mitteilung über quantitative organische Analyse—XXXIV: Beitrag zum Studium der Methode zur Bestimmung von Sauerstoff in organischen Substanzen: M. VECERA, J. LAKOMY and L. LEHAR. (13 *June* 1962).

Quantitative treatment of exchange equilibria involving complexans—III: Chelatometric determination of calcium in the presence of magnesium with EGTA: GENKICHI NAKAGAWA, MOTOHARU TANAKA and HIROKA WADA. (18 *June* 1962).

Sur une réaction colorée des carbamates non substitués a l'azote: Applications analytiques et pharmaceutiques: G. DEVAUX, P. MESNARD et MADAME J. CREN. (18 *June* 1962).

Thermoanalytical investigations on high temperature fusion reactions: L. ERDEY and S. GAL. (19 *June* 1962).

Indirect polarographic determination of silver: M. KOPANICA and R. PŘIBIL. (20 *June* 1962).

Precipitation from mixed solvents—I: Aluminium 8-hydroxyquinolate: LESTER C. HOWICK and JERRY L. JONES. (25 *June* 1962).

Application of the radioactive ionisation detector for the analysis of permanent gases by gas chromatography, and some uses in studies of chemical kinetics: A. K. GALWEY. (25 *June* 1962).

Talanta, 1962, Vol. 9, pp. 755 to 760. Pergamon Press Ltd. Printed in Northern Ireland

ANALYTICAL APPLICATIONS OF SECOND ORDER ELECTRODES

JOHN O. FROHLIGER* and RONALD T. PFLAUM
Department of Chemistry, State University of Iowa, Iowa City, Iowa, U.S.A.

(*Received* 5 *February* 1962. *Accepted* 20 *April* 1962)

Summary—Second order electrodes of silver-silver bromide, silver-silver iodide, silver thiocyanate, silver-silver chromate and silver-silver tetraphenylboron have been investigated. Suitable electrodes for the last two systems could not be prepared. The indicator electrodes were coupled with a saturated calomel reference electrode and the potentials of various solutions measured. The response of the electrodes to anion activities was determined and compared with calculated potentials. The effects of ionic strength and diverse ions on the observed potentials were determined. Results on selected samples indicate that direct potentiometric measurements can be used for the determination of bromide, iodide and thiocyanate ions in aqueous solution. In the concentration range of $1 \times 10^{-1} - 1 \times 10^{-4} M$, measurements can be made with an accuracy comparable to that obtained in usual potentiometric work.

INTRODUCTION

A NON-DESTRUCTIVE method of analysis which has found little analytical application is the method of direct potentiometry using second order indicator electrodes. Development of the method has been hindered by the lack of suitable indicator electrodes and insufficient data on the activity coefficients of many ions. However, Chanin[1] recently was successful in determining chloride ion in biological fluids with a silver, silver chloride-mercury^{I}, mercury^{I} sulphate electrode system. He reported that the indicator electrode was useful over the concentration range of 0·1–1·0 mequiv/l. of chloride ion, but that the potential of the cell was unstable. Helmkamp and coworkers[2] analysed chlorinated insecticide residues with a silver-silver chloride indicator electrode and a saturated calomel reference electrode at 40°. In 1958, Stern and coworkers[3] used a silver-silver chloride inidcator electrode and a saturated calomel reference electrode with a Beckman Model G pH meter. The system was used for the determination of chloride ion in samples of sweat, urine and cerebrospinal fluid. In this work, the authors related the activity of chloride ion to the observed cell potential and developed the concept of pCl analogous to pH. Work similar to that of Stern and coworkers on the chloride system has been carried out on the bromide system.[4] The authors investigated the response of a silver-silver bromide indicator electrode and a saturated calomel reference electrode to bromide ion and developed a method for the direct potentiometric determination of bromide ion in aqueous solutions.

In this paper, electrode systems that respond to bromide, iodide and thiocyanate ions are described. Electrode systems that would respond to chromate and tetraphenylborate ions were investigated. Data are presented for the performance of the bromide, iodide and thiocyanate electrodes under varying conditions of ionic strength

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and diverse ion concentrations. The analytical possibilities of these direct potentiometric measurements are discussed.

EXPERIMENTAL

Apparatus

All potential measurements were made with a Beckman Model G pH meter equipped with the appropriate second order indicator electrode and a Beckman No. 1170 asbestos fibre calomel reference electrode at 25°. A Beckman No. 1281 platinum electrode with a shielded lead or a platinum bead sealed in a soft-glass envelope equipped with a shielded lead (leads from discarded glass electrodes are convenient for this purpose) forms the base of the indicator electrode.

Reagents

Analytical grade potassium bromide, potassium iodide, and potassium thiocyanate were obtained from the Mallinckrodt Chemical Works and were used as received. Potassium argentocyanide was prepared according to recommended procedures.[5,6] All other chemicals used were of reagent grade quality.

Preparation of the indicator electrodes

The platinum bead electrodes were silver plated in an electrolysis cell containing a 10% solution of cyanide-free potassium argentocyanide.[6] The resulting silver electrode was washed first with 6*M* ammonia solution, then with distilled water to remove decomposition products from the electroplating process. Second order electrodes for the bromide, iodide and thiocyanate systems were prepared by anodising the silvered beads for 15 sec in acidic solutions of the potassium salt of the respective anion. The anion concentrations were approximately 1*M*. The resulting electrodes were thoroughly washed with distilled water. The electrodes were stored in 1*M* solutions of the respective anions when not in use.

Potential measurements with second order electrodes

A 300-ml tall-form beaker fitted with a rubber stopper to hold the electrodes was used as the cell vessel. A magnetic stirrer was used to stir the solutions. The electrodes were rinsed twice with portions of the test solution prior to measurement. Separate aliquots of the solution were used for measurement. Potential readings were taken at 1-min intervals on quiescent solutions until reproducible readings were obtained.

RESULTS AND DISCUSSION

Physical characteristics of the indicator electrode

The platinum beads, which form the base of the indicator electrodes, had an exposed surface area of about 3 mm^2. The silver deposit adhered firmly to the platinum beads and had a smooth dull grey appearance. The anodised electrodes varied in appearance with the silver salt deposited. The anodised layers adhered firmly to the silver deposit, but could be removed by direct contact with cleansing tissue. For this reason, the electrode surfaces were not wiped dry between measurements.

Because of the small surface area of the electrodes, they can easily be polarised by the passage of a very small current. Since a potentiometer passes sufficient current at all times except at the balance point to polarise the electrodes, this instrument was impractical as a measuring device. The current drawn by a vacuum tube voltmeter causes negligible polarisation of the small electrodes. For this reason, a pH meter was used for all potential measurements. The use of this instrument necessitated the use of shielded electrode leads in order to observe stable readings.

The silver-silver bromide electrodes functioned with no change in potential for a period of 6 months. There is apparently no effect of sunlight, artificial light, or ageing with these electrodes. The silver-silver iodide electrodes, which were originally yellow in colour, darkened to blue after about 6 weeks and required replating. The

silver-silver thiocyanate electrodes functioned for about 1 month, then portions of the silver-silver thiocyanate deposit loosened and fell off the electrode.

Response of the indicator electrodes

The electrical characteristics of the indicator electrodes were determined from the cell

$$Ag, Ag\,X \mid X^- (xM) \parallel KCl(sat) \mid Hg_2Cl_2, Hg.$$

The potential of the cell at 25° is expressed as

$$E\ cell = E°(Ag^+, Ag) + 0{\cdot}05916 \log K_{AgX} - 0{\cdot}05916 \log a_{(x-)} + Ej - E_{SCE}.$$

In this work, E° was taken to be 0·7995 V and E_{SCE} as 0·245 V. Values of $6{\cdot}0 \times 10^{-13}$, $9{\cdot}5 \times 10^{-17}$ and $1{\cdot}2 \times 10^{-12}$ were used for the ion products of silver bromide,

TABLE I.—POTENTIAL VALUES FOR POTASSIUM BROMIDE SOLUTIONS AT 25°

Concn. KBr, *M*	$-\log a_{(Br^-)}$	E.m.f. (calc.), *mV*	E.m.f. (obs.), *mV*	Δ e.m.f. *mV*
$1{\cdot}95 \times 10^{-1}$	0·846	−118	−116	−2
$8{\cdot}46 \times 10^{-2}$	1·178	−98	−99	+1
$4{\cdot}72 \times 10^{-2}$	1·412	−85	−84	−1
$1{\cdot}89 \times 10^{-2}$	1·782	−63	−64	+1
$7{\cdot}56 \times 10^{-3}$	2·159	−41	−39	−2
$3{\cdot}78 \times 10^{-3}$	2·452	−24	−25	+1

iodide, and thiocyanate, respectively. These are averages of the values tabulated by Schwarzenbach.[7] Activity coefficients used in the log $a_{(x^-)}$ values were obtained from Latimer's tables.[8] Cell potentials were calculated neglecting the contribution of the liquid junction potential.

Comparisons were made between the calculated potentials and the measured potentials of solutions of known anion concentration. The data for the bromide and iodide systems are presented in Tables I and II. The observed potential values

TABLE II.—POTENTIAL VALUES FOR POTASSIUM IODIDE SOLUTIONS AT 25°

Concn. KI, *M*	$-\log a_{(I^-)}$	E.m.f. (calc.), *mV*	E.m.f. (obs.), *mV*	Δ e.m.f., *mV*
$1{\cdot}05 \times 10^{-1}$	1·076	−329	−330	+1
$5{\cdot}25 \times 10^{-2}$	1·326	−314	−314	0
$2{\cdot}10 \times 10^{-2}$	1·733	−290	−292	+2
$1{\cdot}05 \times 10^{-2}$	2·022	−273	−274	+1
$5{\cdot}25 \times 10^{-3}$	2·282	−257	−255	−2
$2{\cdot}10 \times 10^{-3}$	2·699	−233	−232	−1
$1{\cdot}05 \times 10^{-3}$	2·996	−215	−215	0

presented here and in the following tables represent the averages of replicate readings on at least two identical aliquots of the test solution. A deviation of 2 mV obtained between the observed and calculated potentials is the limit of sensitivity of the meter. The potentials listed in the tables show that the electrodes respond to the activity of the anion and that the liquid junction potential is less than the meter error and can be neglected. Although activity coefficients are not available for the thiocyanate system, the thiocyanate electrode did respond to changes in the thiocyanate concentration in the manner predicted by the Nernst equation.

Effect of ionic strength

In order to utilise second order electrodes in an analytical application, the measured potential should be related to concentration rather than to activity. For any system, there is a limited region of ionic strength in which the activity coefficient of a particular anion will be invariant. In this concentration range, usually achieved by the addition of a high concentration of an inert electrolyte, a direct relationship between potential and concentration is permissible. Table III shows the effect of varying concentrations

TABLE III.—EFFECT OF IONIC STRENGTH ON THE RESPONSE OF SECOND ORDER INDICATOR ELECTRODES

Anion concn., *M*	Cell potentials, *mV*					
	Concn. KNO_3, *M*					
	0	0·2	0·6	1·0	1·4	1·8
9·45 × 10^{-3} KBr	−56	−46	−40	−36	−36	−34
1·05 10^{-2} KI	−276	−268	−264	−262	−262	−261
7·68 10^{-3} KSCN	−39	−31	−27	−25	−24	−23

of potassium nitrate on the potentials of bromide, iodide and thiocyanate solutions. At concentrations of potassium nitrate of 1·0–1·4*M*, the activity coefficient of the measured anion is essentially constant since constant potential values were obtained. These potentials can then be expressed as

$$E \text{ cell} = E' - 0{\cdot}0591 \log [X^-]$$

where E′ is the summation of all constant terms in the Nernst equation.

Effect of diverse ions

It was found that the bromide, iodide and thiocyanate electrodes responded equally well in both acidic and basic solutions. No effect of hydrogen ion was noted over a pH range of 1 to 11. Naturally, bromide ion interferes in the thiocyanate system, iodide in the bromide and thiocyanate systems, and thiocyanate in bromide solutions. Oxidising agents, such as dichromate and permanganate ions, act as interferences in all three systems. Cyanide and thiosulphate ions form soluble silver complexes and interfere in the measurements. Other common anions have no effect in concentrations of 2000 ppm.

The three systems studied are relatively free of cationic interferences. The presence of metallic ions which form complexes or insoluble salts with the anion being measured leads to errors. Thus, iron^{III} ion is undesirable in a thiocyanate solution and copper^{II} ion in an iodide system.

Analytical applications of the indicator electrodes

The determination of bromide ion, iodide ion and thiocyanate ion can be carried out using a silver-silver bromide, silver-silver iodide and a silver-silver thiocyanate indicator electrode, respectively.

Weighed samples of the anion are dissolved in distilled water and potassium nitrate added so that the final concentration of potassium ion in the solution is 1*M*. The solution is brought to constant temperature at 25°. The pH of the final solution should be between 1 and 11. The potential of the solution is then measured as previously described. The concentration of the anion is determined from a calibration curve constructed from potential measurements on solutions of known concentration.

The results of measurements on a series of synthetic samples of bromide, iodide and thiocyanate ions are shown in Table IV. The potential of the solutions can be measured with an accuracy of 2 mV. A 1-mV deviation in the potential measurement will cause a deviation of 3 to 5% in the determination of the concentration of the solution. Best results are obtained in the concentration range of 1×10^{-1} to 1×10^{-4}M.

Determination of pSCN

The use of the pH scale of the pH meter has been recommended for the potentiometric measurements of solutions of chloride[3] and bromide[4] ions. The use of the pH scale of the meter increases the sensitivity of the instrument by a factor of 100 to 59. The zero adjust control compensates for slight variation in the individual indicator

TABLE IV.—RESULTS ON SELECTED SAMPLES IN 1*M* POTASSIUM NITRATE AT 25°

Sample	E.m.f. (obs.), *mV*	Concn. X^- present, *M*	Concn. X^- found, *M*
KBr	−92	$8{\cdot}17 \times 10^{-2}$	$8{\cdot}20 \times 10^{-2}$
KBr	−75	$4{\cdot}72 \times 10^{-2}$	$4{\cdot}70 \times 10^{-2}$
KBr, NaCl	−51	$1{\cdot}89 \times 10^{-2}$	$1{\cdot}85 \times 10^{-2}$
KBr, NaF	−4	$2{\cdot}83 \times 10^{-3}$	$2{\cdot}90 \times 10^{-3}$
KBr, K_2SO_4	+20	$9{\cdot}45 \times 10^{-4}$	$1{\cdot}05 \times 10^{-3}$
KI	−304	$5{\cdot}25 \times 10^{-2}$	$5{\cdot}40 \times 10^{-2}$
KI	−283	$2{\cdot}45 \times 10^{-2}$	$2{\cdot}55 \times 10^{-2}$
KI, NaCl	−236	$4{\cdot}20 \times 10^{-2}$	$4{\cdot}21 \times 10^{-2}$
KI, KF	−218	$2{\cdot}10 \times 10^{-3}$	$2{\cdot}00 \times 10^{-3}$
KI	−199	$1{\cdot}05 \times 10^{-3}$	$9{\cdot}50 \times 10^{-4}$
KSCN	−67	$3{\cdot}84 \times 10^{-2}$	$4{\cdot}00 \times 10^{-2}$
KSCN	−35	$1{\cdot}15 \times 10^{-2}$	$1{\cdot}15 \times 10^{-2}$
KSCN, NaCl	−25	$7{\cdot}68 \times 10^{-3}$	$7{\cdot}60 \times 10^{-3}$
KSCN, K_2SO_4	−1	$3{\cdot}00 \times 10^{-3}$	$3{\cdot}07 \times 10^{-3}$
KSCN	+17	$1{\cdot}54 \times 10^{-3}$	$1{\cdot}50 \times 10^{-3}$

electrodes. The potentials of iodide ion solutions are too large to be measured on the pH scale of the meter. However, the potentials of solutions of thiocyanate ion can be measured. The value of 11 on the pH scale was chosen as a convenient value for a 1*M* solution of thiocyanate ion concentration or zero pSCN. In order to use the pH scale, the meter must be standardised. A solution of known thiocyanate ion concentration is used to standardise the meter. For example, a 0·1*M* solution of

TABLE V.—pSCN VALUES FOR THIOCYANATE SOLUTIONS

Concn. SCN^-, *M*	Meter reading	pSCN (calc.)	pSCN (obs.)
$3{\cdot}84 \times 10^{-2}$	9·60	1·42	1·40
$1{\cdot}54 \times 10^{-2}$	9·14	1·81	1·86
$7{\cdot}68 \times 10^{-3}$	8·89	2·11	2·11
$3{\cdot}84 \times 10^{-3}$	8·60	2·42	2·40
$1{\cdot}54 \times 10^{-3}$	8·08	2·81	2·92
$7{\cdot}68 \times 10^{-4}$	7·72	3·11	3·28

thiocyanate ion concentration would have a pSCN of 1 and the meter would then be standardised at 10 on the pH scale; for a 0·01*M* solution, the meter would read 9.

In general, pSCN is equal to 11-scale reading. The results in Table V show the determination of thiocyanate ion solutions using the pH scale of the meter. The accuracy obtained in these measurements is comparable to that obtained in pH measurements.

Zusammenfassung—Elektroden zweiter Ordnung wie Ag-AgBr, Ag-AgJ, AgCSN, Ag-Ag_2CrO_4 und Ag-AgTetraphenylborat wurden hergestellt. Die Indicatorelektroden wurden gegen eine ges. Calomelelektrode geschaltet und die Potentiale verschiedener Lösungen gemessen. Das Ansprechen der Elektroden auf Anionenaktivitäten wurde ermittelt und mit berechneten Potentialen verglichen. Der Einfluss der Ionenstärke und verschiedener Ionen wurde studiert. Ergebnisse mit ausgewählten Systemen zeigen, dass direkte potentiometrische Messungen zur Bestimmung von Bromiden, Jodiden und Rhodaniden in wässriger Lösung angewendet werden können. Im Konzentrationsbereich 10^{-1}— 10^{-4} sind die Messungen etwa von gleicher Genauigkeit wie in üblicher potentiometrischer Arbeitsweise.

Résumé—Les auteurs ont préparé des électrodes du deuxième genre: argent-bromure d'argent, argent-iodure d'argent, thiocyanate d'argent, argent-chromate d'argent et argent-tétraphénylborate d'argent. Les électrodes indicatrices sont couplées avec une électrode de référence au calomel saturée et les potentiels de diverses solutions sont mesurés. La réponse des électrodes aux activités de l'anion est déterminée et comparée aux potentiels calculés. Les effets de la force ionique et des différents ions sur les potentiels observés sont déterminés. Les résultats, pour des échantillons sélectionnés, indiquent que l'on peut utiliser des mesures potentiométriques directes pour le dosage des ions bromure, iodure et thiocyanate en solution aqueuse. Dans le domaine de concentration 10^{-1} à 10^{-4} M, des mesures peuvent être faites avec une précision comparable à celle obtenue dans une étude potentiométrique usuelle.

REFERENCES

[1] M. Chanin, *Science*, 1954, **119**, 323.
[2] G. K. Helmkamp, F. A. Gunther, J. P. Wolf, III and J. E. Leonard, *J. Agric. Food Chem.*, 1954, **2**, 836.
[3] M. Stern, H. Shwachman, T. S. Licht and A. J. deBethune, *Analyt. Chem.*, 1958, **30**, 1506.
[4] J. O. Frohliger and R. T. Pflaum, Paper presented at the 139th Meeting of the American Chemical Society, St. Louis, Mo., March, 1961.
[5] H. Bassett and A. S. Corbet, *J. Chem. Soc.*, 1924, **125**, 1660.
[6] A. S. Brown, *J. Amer. Chem. Soc.*, 1934, **56**, 646.
[7] G. Schwarzenbach, J. Bjerrum and L. G. Sillen, *Stability Constants of Metal Ion Complexes.* The Chemical Society, London, 1957.
[8] W. M. Latimer, *The Oxidation States of the Elements and Their Properties in Aqueous Solutions.* Prentice-Hall, Inc., New York, 2nd., 1952.

Talanta, 1962, Vol 9, pp. 761 to 767. Pergamon Press Ltd. Printed in Northern Ireland

SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM AND PLATINUM WITH DIBENZYLDITHIO-OXAMIDE*

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Summary—Palladium^{II} and platinum^{II} form water-insoluble coloured complexes with dibenzyldithio-oxamide which are extractable into chloroform. Factors affecting the analytical use of this reagent have been investigated. The yellow palladium complex and the rose-coloured platinum complex show absorption maxima at 450 and 520 mμ, respectively. Beer's law is obeyed over the range investigated, and a close control of conditions of colour development is not necessary. The tolerance to a number of diverse ions has been established with favourable results. A procedure for the simultaneous determination of palladium and platinum has been developed.

INTRODUCTION

IN a recent study of a series of substituted dithio-oxamides,[1] it was found that the dibenzyl derivative showed promise of being a good reagent for the spectrophotometric determination of palladium and platinum. This derivative was selected for further investigation because of favourable absorbance curves for the palladium and platinum complexes and the sensitivities of the colour reactions. Xavier and Rây[2] have investigated dibenzyldithio-oxamide as a colorimetric reagent for certain elements of the transitional series, but these workers presented no quantitative data concerning palladium and platinum. Examination of the literature will reveal that there are many reagents proposed for the spectrophotometric determination of palladium and/or platinum. However, many of these require a close control over conditions of colour development, many are time consuming, and many require the complexation of diverse ions with agents such as EDTA if interference is to be minimised. Because of freedom from the control of variables and the simplicity of the colour reaction, dibenzyldithio-oxamide is proposed as a reagent which could find application in rapid, routine analyses for palladium and platinum.

EXPERIMENTAL

Apparatus

Spectrophotometer: All absorbance measurements were made with a Beckman Model DU spectrophotometer using matched silica cells of 1-cm light path.

Separatory funnels: Globe Separatory funnels of 125-ml volume, and stems shortened to approximately 1 cm were used for all extractions.

Reagents

Standard palladium solution: Prepared by dissolving about 1 g of palladium^{II} chloride in 500 ml of distilled water containing sufficient hydrochloric acid to give a final concentration 1*M* in the acid.

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The palladium content was determined to be 1·15 mg/ml by the dimethylglyoxime gravimetric method.

Standard platinum solution: Prepared by dissolving about 7 g of chloroplatinic acid hexahydrate in 1 litre of distilled water with sufficient hydrochloric acid to give a final concentration 1*M* in the acid. The platinum content was determined gravimetrically by reducing the platinum to the metal with formic acid. The standard solution contained 2·83 mg of platinum per ml.

Reagent solution: Prepared by dissolving 1·00 g of dibenzyldithio-oxamide in 100 ml of acetone. The reagent, obtained from the Aldrich Chemical Company, Incorporated, Milwaukee, Wisconsin, was used without further purification. The solution was found to be stable for at least 3 weeks. Longer periods of time were not investigated.

Solutions of diverse ions: Stock solutions containing 1 mg/ml of the ion were prepared from nitrates or chlorides of the metal, except osmium, which was prepared from potassium osmate.

All other reagents were analytical grade, used without further purification.

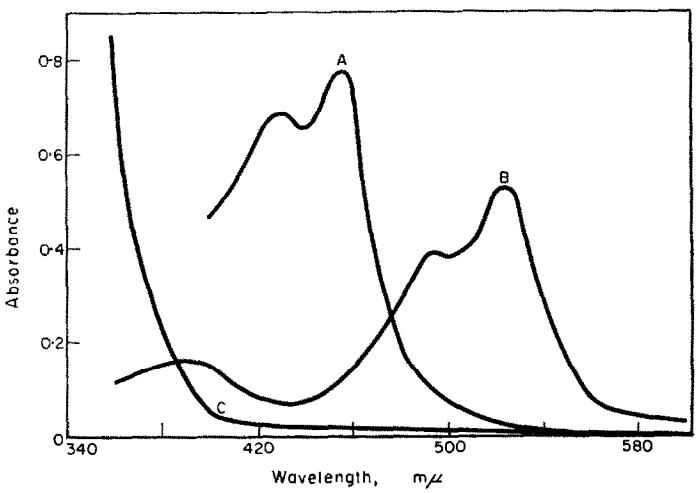


FIG. 1.—Absorbance curves for the palladium complex, platinum complex, and reagent:
(A) 4·2 ppm of palladium,
(B) 3·4 ppm of platinum,
(C) reagent, 6·6 × $10^{-3}M$.

Complex formation

Quadrivalent platinum reacts very slowly with the reagent in strong hydrochloric acid solution. However, when platinum^{IV} is reduced to platinum^{II}, the reaction proceeds fairly rapidly at room temperature, maximum colour intensity being attained in about 30 min. With palladium, the reaction is apparently instantaneous. One ml of 2*M* sodium sulphite solution, followed by hydrochloric acid, effects the reduction of platinum^{IV}. This treatment has no influence on the palladium complex formation.

Absorbance curves

The water-insoluble complexes of palladium and platinum are readily extractable into chloroform. In Fig. 1 are shown the absorbance curves for the chloroform solutions of the yellow palladium complex (4·2 ppm), the rose-coloured platinum complex (3·4 ppm), and the reagent (6·6 × $10^{-3}M$). In the case of both palladium and platinum, the colour was allowed to develop for 0·5 hr in approximately 9*M* hydrochloric acid before extraction. The maxima for palladium and platinum are 450 and 520 mμ, respectively. The reagent shows negligible absorbance above 425 mμ. The absorbances of the palladium and platinum complexes were measured against a reagent blank; the absorbance of the reagent was measured against chloroform.

Hydrochloric acid concentration

Fig. 2 shows that colour development is optimum in solutions which have an acid molarity greater than about 8. These results were obtained by varying the acid molarity of the aqueous solutions in which colour developments occurred from 0·77 to 10·0*M*, in the case of palladium, and from 2·5 to 10·6*M*, in the case of platinum. Each palladium sample contained 105·4 μg of palladium, sufficient

concentrated hydrochloric acid to furnish predetermined increasing acid molarities, and 5 ml of the 10 mg/ml reagent solution. The samples were extracted with two 5-ml portions of chloroform, and diluted to 25 ml with chloroform. Each platinum sample contained 85·0 μg of platinum, 1 ml of 2*M* sodium sulphite solution, sufficient concentrated hydrochloric acid to furnish predetermined increasing acid molarities, and 5 ml of the 10 mg/ml reagent solution. The samples were extracted and diluted in the same manner as the palladium samples. The gain in sensitivity realised by increasing the acid molarity in the aqueous phase above 8*M* is so slight that reproducible results are obtained without rigorous control of the acid concentration. In practice, 25–30 ml of concentrated hydrochloric acid are used in a volume of 35–40 ml of solution before extraction.

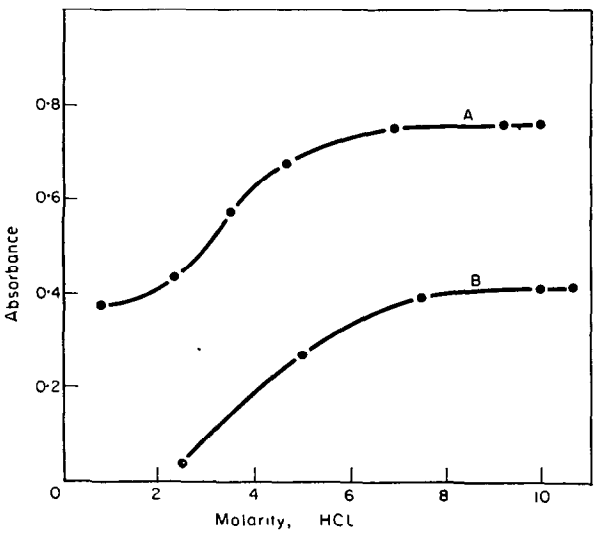


FIG. 2.—Effect of the molarity of hydrochloric acid on the palladium and platinum complexes:
(A) 4·2 ppm of palladium,
(B) 3·4 ppm of platinum.

Rate of colour formation

Studies reveal that the yellow palladium complex forms immediately, while the rose-coloured platinum complex forms more slowly. About 30 min are required for the platinum complex to develop maximum intensity. To determine the optimum time for colour development, samples of palladium and platinum were prepared containing 115·4 μg and 85·0 μg, respectively. The samples were allowed to develop colour for varying lengths of time, after which they were extracted and diluted to 25 ml with chloroform. The absorbances of the palladium and platinum complexes were measured at 450 and 520 mμ, respectively. Table I shows the findings of this experiment.

TABLE I—Rate of colour formation

Time, *min*	Absorbance Pd (450 mμ)	Pt (520 mμ)
Immediately	0·812	0·290
15	0·815	0·405
30	0·815	0·445
45	0·812	0·443
60	0·815	0·446

Stability of colour

In order to investigate the stability of the extracted complexes on standing, the absorbances of a palladium sample and a platinum sample were measured at intervals of 10 min, 45 min, 3 hr, 24 hr and 48 hr. There was no change in absorbances observed over this period of time. Longer periods were not investigated.

Extraction of the complex

Extraction of prepared palladium and platinum complexes with one, two, three, and four 5-ml portions of chloroform, and subsequent determination of absorbances, indicate that the complexes are completely extracted by the use of two 5-ml portions of chlofororm.

Reagent concentration

It is desirable to use a large excess of reagent when determining palladium and/or platinum in the presence of other metals, because certain of these diverse ions appear to consume some of the reagent, even though interferences are not proportionately severe. In practice, 5 ml of the 10 mg/ml reagent

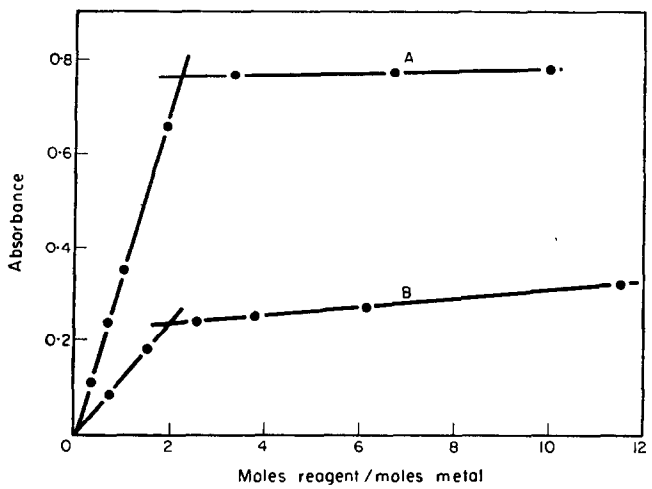


FIG. 3.—Mole ratio method applied to palladium and platinum complexes at 450 and 520 mμ, respectively:
(A) palladium, $3{\cdot}96 \times 10^{-5}M$,
(B) platinum, $1{\cdot}74 \times 10^{-5}M$.

solution are used. For samples containing 115·4 μg of palladium or 85·0 μg of platinum, this concentration of reagent furnishes a molar ratio of reagent to palladium and platinum of about 31:1 and 76:1 respectively.

Conformity to Beer's law

Beer's law is obeyed over the range investigated; 0·92 to 6·93 ppm in the case of palladium, and 0·68 to 5·10 ppm in the case of palladium.

Sensitivity

According to the Sandell notation,[3] the sensitivity of the reaction for palladium is 0·0055 μg per cm^2, and for platinum is 0·0075 μg per cm^2.

Nature of complex in solution

The empirical formulae for the complexes of palladium^{II} and platinum^{II} in solution were established by two independent methods, the mole-ratio method of Yoe and Jones,[4] and the slope-ratio method of Harvey and Manning.[5] The results of these experiments show that 2 moles of the reagent react with 1 mole of the bivalent metal ion. Fig. 3 shows the results of applying the mole-ratio method to the complexes of palladium and platinum at the respective wavelengths of maximum absorbance. The concentration of palladium was held constant at $3{\cdot}96 \times 10^{-5}M$ and that of platinum at $1{\cdot}74 \times 10^{-5}M$. These findings are in accord with earlier investigations of other derivatives of dithio-oxamide.[6,7,8]

Effect of diverse ions

Solutions containing 1 mg of the foreign ion per ml were prepared to determine the effect of selected ions on the colour reaction. These ions were added individually to solutions containing

TABLE II.—Effect of diverse ions on palladium complex*

Ion added	Quantity added, *mg*	Palladium found, *μg*	Error, %
Fe^{III}	5·7	77	−78·0
Fe^{III}†	5·7	110	+4·8
Co^{II}	5·0	106	+0·9
Ni^{II}	5·0	105	0·0
Ru^{III}	4·9	105	0·0
Rh^{III}	3·6	105	0·0
Os^{VI}	1·1	104	−0·9
Ir^{IV}	5·8	114	+8·5
Pt^{IV}	7·5	107	+1·9
Pt^{IV}	0·02	108	+2·9
Cu^{II}	5·0	106	+0·9
Au^{III}	2·5	141	+25·0
Au^{III}†	6·2	107	+1·9
Cr^{III}	5·0	105	0·0

* 105 *μ*g of palladium present.
† These samples contained approximately 1 ml of 1*M* sodium sulphite.

TABLE III.—Effect of diverse ions on platinum complex*

Ion added	Quantity added, *mg*	Platinum found, *μg*	Error, %
Fe^{III}	1·0	79	−7·1
Co^{II}	0·5	80	−6·3
Ni^{II}	0·2	82	−3·5
Ru^{III}	1·0	90	+5·9
Rh^{III}	1·9	82	−3·5
Pd^{II}	0·06	88	+3·5
Os^{VI}	0·05	81	−4·6
Ir^{IV}	1·8	89	+4·7
Cu^{II}	0·2	81	−4·6
Au^{III}	2·2	79	−7·0
Cr^{III}	0·2	79	−7·0

* 85 *μ*g of platinum present.

105·4 *μ*g of palladium, and to solutions containing 85·0 *μ*g of platinum. The palladium samples were extracted immediately while the platinum samples were allowed to develop colour for 30 min. An interference is arbitrarily chosen as that concentration which would give an error of greater than 3% in the amount of palladium or platinum found after extraction and dilution. The results of these findings are shown in Tables II and III.

Determination of palladium

Because the colour reaction with palladium is apparently instantaneous, the complex formed can be extracted immediately into chloroform. This technique obviates diverse ion interference markedly, because most of these ions do not form complexes immediately. A recommended procedure is as follows:

Introduce an aliquot of the sample (not over 5 ml), containing between 25 and 100 *μ*g of palladium and no foreign ions in excess of those which would give a 3% error (see Table II), into a 125-ml separatory funnel. Add 25–30 ml of concentrated hydrochloric acid and 5 ml of the 10 mg/ml reagent solution. Swirl the funnel for a few sec, introduce about 5 ml of chloroform, stopper, and shake vigorously for about 10 sec. Let the layers separate, and draw the organic phase into a 25-ml volumetric flask. Repeat the extraction procedure, and bring the flask up to volume with chloroform. Measure the absorbance at 450 m*μ* against a reagent blank and determine the palladium content from a calibration curve.

Determination of platinum

Introduce an aliquot of the sample (not over 5 ml), containing between 35 and 135 *μ*g of platinum and no foreign ions in excess of those which would give a 3% error (see Table III), into a 125-ml

separatory funnel. Add 1 ml of 2*M* sodium sulphite solution, swirl, then add about 25–30 ml of concentrated hydrochloric acid. The order of this addition must not be reversed. Swirl the funnel again for a few sec and add 5 ml of the 10 mg/ml reagent solution. Allow 30 min for colour development with periodic swirling. Introduce about 5 ml of chloroform, stopper, and shake vigorously for about 10 sec. Let the layers separate and draw the organic phase into a 25-ml volumetric flask. Ignore the sulphite precipitate which may form, but remains in the aqueous phase. Repeat the extraction procedure and bring the flask up to volume with chloroform. Measure the absorbance of the sample at 520 mμ against a reagent blank and determine the platinum content from a calibration curve.

Simultaneous determination of palladium and platinum

The absorbance curves for the complexes of palladium and platinum, shown in Fig. 1, represent an almost ideal situation for the simultaneous determination of the two metals. At the wavelength of maximum absorbance shown by palladium, there is little absorbance from the platinum complex, and *vice versa*. Spectrophotometric equations may be derived from known values of the molar absorptivities of the palladium and platinum complexes, enabling one to calculate the concentrations of palladium and platinum from absorbance measurements made at 450 and 520 mμ.[9] For the equations to be valid, the absorbances of the complexes of palladium and platinum must be additive at the two wavelengths of consideration. In addition, Beer's law must be obeyed by the two complexes at both wavelengths. Both of these conditions have been verified experimentally. Molar absorptivities of the palladium and platinum complexes used for calculation of the spectrophotometric equations, and the equations derived from these values are given in Table IV. A recommended procedure

TABLE IV—Molar absorptivities of platinum and palladium complexes

	450 Mμ	520 Mμ
ϵ Pd	19,000	737
ϵ Pt	4,900	25,500

Equations derived from above values:
$(Pd) \times 10^5 = 5{\cdot}32\ A_{450} - 1{\cdot}02\ A_{520}$,
$(Pt) \times 10^5 = 3{\cdot}96\ A_{520} - 0{\cdot}154\ A_{450}$.

for the simultaneous determination of palladium and platinum is identical to the determination of platinum alone, except that measurements are made at both 450 and 520 mμ. The molar concentrations of palladium and platinum may then be calculated with the aid of equations given in Table IV.

The results of the analysis of a series of synthetic samples by this procedure are shown in Tables V and VI.

TABLE V—Simultaneous analysis of synthetic samples

Pd, μg		Pt, μg	
Added	Found	Added	Found
23·1	22·9	85·0	85·0
57·8	59·2	85·0	85·0
115	117	85·0	83·0
115	115	17·0	15·5
115	115	42·5	39·5
11·5	11·5	34·0	34·5
46·2	47·8	128	129
23·1	23·7	128	127
11·5	11·6	68·0	67·0
59·8	58·3	8·5	7·8
11·5	11·0	8·5	7·7
11·5	10·3	85·0	84·8

CONCLUSIONS

Dibenzyldithio-oxamide has been shown to react with palladium and platinum in strong hydrochloric acid solutions to form water-insoluble complexes which may be

TABLE VI—Simultaneous analysis of synthetic samples

Sample no.	Pd, μg		Pt, μg		Diverse ions, *mg*
	Added	Found	Added	Found	
1	115	117	25·5	15·4	Ir, 0·45 Ru, 0·49 Rh, 0·52
2	23·1	24·9	128	129	Same as sample 1
3	23·1	25·8	25·5	13·0	Fe, 0·50 Co, 0·50 Ni, 0·50 Cu, 0·50
4	115	117	128	119	Same as sample 3

extracted with chloroform. Conditions for the development of colour do not have to be rigorously controlled. The reagent has a sensitivity for palladium and platinum which compares favourably with other reagents for these metals. The simplicity of the analytical procedure, and the favourable tolerance for other platinum metals and certain base metals are advantages to be considered in employing this reagent for palladium and platinum.

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Zusammenfassung—Palladium(II) und Platin(II) bilden wasserunlösliche, gefärbte Komplexe mit Dibenzyldithio-oxamid, Die Komplexe können mit Chloroform extrahiert werden. Faktoren, die die analytische Anwendung des Reagenses beinflussen, werden untersucht. Der gelbe Palladiumkomplex hat ein absorptionsmaximum bei 450 mμ, der rosa Platinkomplex bei 520 mμ. Beer's Gesetz wird über einen weiten Konzentrationsbereich befolgt; strenges Einhalten der Bedingungen ist nicht nötig. Eine Anzahl verschiedener Ionen übt keine Störung aus. Eine Methode zur gleichzeitigen Bestimmng von Palladium und Platin wurde ausgearbeitet.

Résumé—Le palladium(II) et le platine(II) forment des complexes colorés, insolubles dans l'eau, avec le dibenzyldithio-oxamide; des complexes peuvent être extraits par le chloroforme. Les auteurs ont étudié les facteurs influant sur l'utilisation analytique de ce réactif. Le complexe du palladium jaune et celui du platine rose montrent des maxima d'absorption respectivement à 450 et 520 mμ. La loi de Beer est suivie dans le domaine étudié, et un contrôle approfondi des conditions de développement de la couleur n'est pas nécessaire. La tolérance à un certain nombre d'ions variés a été établie avec des résultats favorables. Une méthode de dosage simultané du palladium et du platine a été mise au point.

REFERENCES

[1] W. D. Jacobs and J. T. Pyle, unpublished studies.
[2] J. Xavier and P. Rây, *J. Indian Chem. Soc.*, 1958, **35**, 725.
[3] E. B. Sandell, *Colorimetric Determination of Traces of Metals*. Interscience Publishers, New York, 3rd Ed., 1959, p. 83.
[4] J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Analyt.*, 1944, **16**, 111.
[5] A. E. Harvey and D. L. Manning, *J. Amer. Chem. Soc.*, 1950, **72**, 4488.
[6] W. D. Jacobs, *Analyt. Chem.*, 1960, **32**, 512.
[7] *Idem, ibid.*, 1961, **33**, 1279.
[8] W. D. Jacobs, Clara M. Wheeler and W. H. Waggoner, *Talanta*, 1962, **9**, 243.
[9] E. B. Sandell, *op cit.*, p. 103.

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COMPLEXOMETRIC DETERMINATION OF COPPER IN THE PRESENCE OF OTHER IONS

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Summary—Copper^{II} ions form stable complexes with EDTA, whereas copper^{I} ions do not. Thus, if the copper^{II} in a copper^{II}-EDTA complex is reduced to copper^{I}, an equivalent quantity of EDTA is liberated. To a solution containing copper^{II} and other ions an excess of EDTA is added, the solution is brought to pH 5·5–6·0 and titrated with lead nitrate solution in the presence of Xylenol Orange as indicator. At this pH all ions forming stable complexes, including copper^{II}, are firmly associated. Thiourea is then used for the reduction of copper^{II} to copper^{I} in a strongly acidic media where the copper^{II}-EDTA complex is dissociated. The solution is re-adjusted to pH 5·5–6·0 and the liberated EDTA titrated with lead nitrate solution. Most common ions (Ag^{I}, Pb^{II}, Zn^{II}, Ni^{II}, Bi^{III}, Sb^{III}, As^{III}, Fe^{III}, Al^{III}, Sn^{IV}, *etc.*) do not interfere with the determination. The present method has been used successfully for the determination of copper in copper alloys, concentrates and minerals.

THE fact that copper^{II} forms stable complexes with EDTA[1] has been used for its easy and precise determination by complexometric titration. Because the reaction of EDTA with copper^{II} is not selective, most of the proposed complexometric methods necessitate the preliminary separation of copper^{II} from all other ions.[2,3] A few methods are available by which the determination of copper is possible in the presence of only one or two other ions, the interference of the latter being eliminated by a suitable masking agent.[4,5,6,7,8]

Many univalent ions do not form stable EDTA-complexes, so that their presence does not interfere with the complexometric determination of bi- and tervalent ions. The stability constant of the copper^{I}–EDTA complex is not known, but its value is small. This permits the determination of many bivalent ions in the presence of copper^{I}. Thus a method for the determination of zinc in brass has been devised, using thiosulphate as a reducing and masking agent for copper^{II}.[4]

The different behaviour of copper^{II} and copper^{I} in respect to EDTA is used in the present paper to develop a complexometric method for the determination of copper^{II} in the presence of other ions, based on reduction of the copper^{II} in a copper^{II}-EDTA complex to copper^{I} and titration of the liberated EDTA.

EXPERIMENTAL

Reagents

0·05*M EDTA solution:* Prepared by dissolving 37·22 g of Chelaton 3 (Chemapol, Prague) in 2 litres of distilled water. The solution was standardised against copper (E. Merck AG) in dilute ammonia solution (pH 7·5–8·0) using murexide as indicator.

0·05*M Copper^{II} nitrate solution:* Prepared by dissolving 24·16 g of $Cu(NO_3)_2.3H_2O$ (analytical grade) in 2 litres of distilled water. The solution was standardised against 0·05 *M* EDTA solution in a slightly alkaline medium, as described above.

0·025*M Lead nitrate solution:* Prepared by dissolving 16·52 g of $Pb(NO_3)_2$ (analytical grade) in 2 litres of distilled water and standardised against 0·05*M* EDTA solution at pH 5·5–6·0 using Xylenol Orange as indicator.[9]

10% *Thiourea solution:* Prepared by dissolving 100 g of thiourea (analytical grade) in 1 litre of cold distilled water and then filtered.

Acetate buffer solution (pH 5·5–6·0): Dilute 95 ml of glacial acetic acid (analytical grade) with 500 ml of distilled water, then add 135 ml of ammonia solution (analytical grade, sp. gr. 0·91) and make the solution up to 1 litre with distilled water. When the buffer is diluted ten times the pH of the buffer solution should have a value of 5·5–6·0 (measured with a pH-meter). If necessary it must be corrected.

Xylenol Orange indicator:[9] 0·1 g of Xylenol Orange (Chemapol, Prague) ground with 10 g of potassium nitrate in a porcelain mortar.

Solutions of various ions having a concentration of 10 mg/ml were prepared from salts (analytical grade reagents) of Ag^{I}, Hg^{I}, Hg^{II}, Zn^{II}, Ni^{II}, Cd^{II}, Co^{II}, Mn^{II}, Fe^{II}, Fe^{III}, Sb^{III}, Bi^{III}, As^{III}, Al^{III}, Cr^{III}, Sn^{IV}, Se^{IV}, Te^{IV}, V^{V}, Mo^{VI}, chloride and sulphate. All other reagents were analytical grade.

Apparatus

An officially verified 25-ml burette with 0·05-ml divisions and a sharpened tip covered with solid paraffin was used, thus permiting titration with 0·01-ml drops. The titrated solution was agitated with a magnetic stirrer. All of the volumetric flasks and pipettes were officially verified.

RESULTS

Investigation of the copper^{II}-EDTA reduction

Preliminary experiments indicated that in the presence of EDTA and at pH 5·5–6·0 reduction of the copper^{II}-EDTA complex is incomplete. The following reducing agents were used: thiosulphate, thiourea, thioglycollate, ascorbic acid and sulphite. The incomplete reduction is probably caused by the presence of EDTA which, by associating with copper^{II} in a complex, lowers the redox potential of the copper^{II}/copper^{I} system. The EDTA complexes of bivalent metals are stable in alkaline, neutral or weakly acid media, but not in strongly acidic media. In acidic solutions (pH 0–1) the bivalent ion complexes are dissociated. It is, therefore, to be expected that an increase of hydrogen ion concentration and hence of copper^{II} concentration should result in an improvement of the reduction conditions. Experiments showed that in strongly acidic solution copper^{II} ions are reduced quantitatively to copper^{I} by thiourea in the presence of EDTA and a colourless complex of copper^{I} is formed. Detailed investigations were performed to establish the optimum reduction time, the most suitable thiourea concentration, *etc.*, so that the best conditions for the quantitative determination of copper were found. Based on these experiments the following procedure for the determination of copper is proposed:

To a neutral solution containing 5–50 mg of copper^{II}, add an excess of 0·05*M* EDTA solution, 2 ml of buffer solution (pH 5·5–6·0) and Xylenol Orange indicator*. Titrate with 0·025*M* lead nitrate solution until the colour of the titrated solution just becomes permanently blue. Add 25 ml of 10% thiourea solution, followed by nitric acid (1:1) dropwise until the colour of the solution changes to yellow†. Stir for 10 min, then neutralise with ammonia solution (1:1) until a violet colour appears. Add 5 ml of buffer solution (pH 5·5–6·0). The precipitate of elemental sulphur which is formed is no obstacle to the further analysis. Titrate the liberated EDTA with 0·025*M* lead nitrate solution in the presence of the Xylenol Orange indicator until a colour change from yellow to violet takes place. The volume of 0·025*M* lead nitrate solution used for the second titration is equivalent to the copper^{II} content of the solution.

* The colour of the solution should be green (a mixed colour from the blue of the copper^{II}-EDTA complex and the yellow of the Xylenol Orange). If the solution is blue, it is an indication that the volume of 0·05*M* EDTA solution is insufficient or that the pH is above 6·0.

† The copper^{II}-EDTA complex is dissociated and the blue component disappears.

Interferences

Standardised solutions of different amounts of foreign ions and equivalent amounts of EDTA were added to a solution containing 15·90 mg of copper^{II}. The pH of the solution was adjusted to 5·5–6·0, excess EDTA titrated with 0·025*M* lead nitrate solution and the determination completed as described above.

The results of these investigations are shown in Table I. They indicate that the ions most commonly encountered (Ag^{I}, Zn^{II}, Ni^{II}, Bi^{III}, Sb^{III}, As^{III}, Fe^{III}, Al^{III}, Cr^{III}, Sn^{IV}, *etc.*) over a wide range of concentrations, do not interfere with the determination of copper^{II}. The presence of the lead^{II} used as titrant has no effect on the determination. The influence of magnesium^{II}, calcium^{II} and barium^{II} was not studied, because no interference is to be expected from them. A certain amount of interference was encountered at very high concentrations of foreign ions. This is probably caused by the adverse effect of the large quantities of EDTA (added to complex foreign ions) on the reduction of the copper^{II} ion and also by the increase of the ionic strength of the solution. Aluminium^{III} and tin^{IV} are easily masked as fluoride complexes.

Iron^{II} and cobalt^{II} interfere with the determination and their contents must not exceed 5–10 mg. Cobalt^{II} ions have a negative effect and those of iron^{II} a positive one. The effect of the latter can be diminished by preliminary oxidation of the solution.

Cadmium^{II}, manganese^{II}, mercury^{I} mercury^{II}, vanadium^{V} and molybdenum^{VI} should be absent. Even small quantities of these ions have an unfavourable effect on the results. Manganese^{II} is easily removed as $MnO_2.xH_2O$ by oxidation with persulphate in a nitric acid medium. The effect of mercury^{I} ions could probably be eliminated if they were oxidised to mercury^{II}, then the latter masked with potassium iodide. In the presence of molybdates, the titration could be carried out with a zinc salt instead of lead nitrate solution.

Regarding anions, it was found that chloride and sulphate have no effect, whereas selenium and tellurium are precipitated in the elemental form and make observation of the colour changes in the vicinity of the equivalent point difficult.

Determination of copper in copper alloys, concentrates and minerals

From the results obtained with pure solutions it seemed that the method might be very convenient for the determination of copper in materials rich in copper (above 10%). A number of analyses of copper alloys, a concentrate and a mineral (bornite) were performed. The results are to be seen in Table II. They indicate good reproducibility and agreement with the results obtained by electroanalytical determination.

Procedure for copper alloys: Dissolve 0·1 g of sample in a 100-ml volumetric flask with 5-ml of nitric acid (1 : 1) (in the presence of tin boil the solution for 5 min). Cool the solution, then dilute to the mark with distilled water. Transfer a 25-ml aliquot to a 150-ml beaker and add 15 ml of 0·05*M* EDTA solution and Xylenol Orange indicator. Add ammonia solution dropwise until the green colour of the solution receives a blue tint, then add 2 ml of buffer solution (pH 5·5–6·0) and complete the analysis as described previously.

Procedure for copper concentrates and minerals: Dissolve 0·3–0·5 g of sample in 10 ml of concentrated hydrochloric acid and 5 ml of concentrated nitric acid, then evaporate the resulting solution to a dry residue. Add a further 2–3 ml of nitric acid and repeat the evaporation. Pour over the residue 50 ml of 1% nitric acid solution and boil for 1 min, then filter into a 100-ml volumetric flask. Wash the filter with warm 0·1% nitric acid solution. Cool and made up the solution to the mark with distilled water. Depending on the quantity of copper, transfer an aliquot of 10–20 ml to a beaker, add 0·5 g of ammonium fluoride (to complex aluminium^{III}), then 10–20 ml of 0·05*M* EDTA solution. Boil for 2–3 min and cool. Add Xylenol Orange indicator and neutralise the solution with ammonia solution (1 : 1) until a blue tint appears. Add 2 ml of buffer solution (pH 5·5–6·0) and complete the analysis as described previously.

TABLE I.—RESULTS FOR THE DETERMINATION OF 15·90 MG OF COPPER IN THE PRESENCE OF FOREIGN IONS.

Foreign ion taken, *mg*		Weight ratio of Cu: foreign ion	Cu found, *mg*	Deviation	
				mg	%
Ag^{I}	100	1:6·3	15·76	−0·14	−0·6
Zn^{II}	25	1:1·5	15·95	0·05	0·3
	50	1:3·1	15·91	0·01	0·06
	100	1:6·3	15·93	0·03	0·2
Ni^{II}	10	1:0·6	15·86	−0·04	−0·2
	25	1:1·5	15·76	−0·14	−0·9
	50	1:3·1	15·73	−0·17	−1·1
Bi^{III}	5	1:0·3	15·90	0·00	0·0
	50	1:3·1	15·93	0·03	0·2
	100	1:6·3	15·71	−0·19	−1·2
Sb^{III}	50	1:3·1	15·96	0·06	0·4
	100	1:6·3	15·91	0·01	0·06
As^{III}	100	1:6·3	15·87[a]	−0·03	−0·2
Fe^{III}	10	1:0·6	15·90	0·00	0·0
	20	1:1·2	15·91	0·01	0·06
	30	1:1·9	15·78	−0·12	−0·8
	40	1:2·5	15·74	−0·16	−1·0
Al^{III}	5	1:0·3	15·94[b]	0·04	0·2
	10	1:0·6	15·85[b]	−0·05	−0·3
Cr^{III}	5	1:0·3	15·78	−0·12	−0·7
Sn^{IV}	50	1:3·1	15·79[c]	−0·11	−0·7
	100	1:6·3	15·96[c]	0·06	0·4
Fe^{II}	5	1:0·3	15·91	0·01	0·06
	25	1:1·5	16·10	0·20	1·3
Co^{II}	2	1:0·1	15·92	0·02	0·1
	5	1:0·3	15·74	−0·16	−1·0
	10	1:0·6	15·72	−0·18	−1·1
Cd^{II}	2	1:0·1	16·19	0·29	1·8
	5	1:0·3	16·20	0·30	1·9
	10	1:0·6	16·18	0·28	1·8
	50	1:3·1	76·30	0·40	2·5
Mn^{II}	2	1:0·1	16·22	0·32	2·0
	5	1:0·3	16·34	0·44	2·8
Hg^{II}	10	1:0·6	18·27	2·37	14·9
Hg^{I}	5	1:0·3	—[d]	—	—
Cl^{-}	200	1:12·6	15·91	0·01	0·06
SO_4^{2-}	200	1:12·6	15·95	0·05	0·3
SeO_3^{2-}	1	1:0·06	15·93	0·03	0·2
	5	1:0·3	—[e]	—	—
TeO_3^{2-}	5	1:0·3	—[e]	—	—
VO_3^{-}	5	1:0·3	—[f]	—	—
MoO_4^{2-}	20	1:1·2	—[g]	—	—

[a] A precipitate forms, which disappears during titration.
[b] Preliminary boiling of the solution with ammonium fluoride.
[c] Preliminary boiling of the solution with sodium fluoride.
[d] A black precipitate of elemental mercury appears.
[e] A red precipitate of elemental selenium and tellurium appears.
[f] The solution cannot be titrated because the indicator is blocked.
[g] A precipitate of lead molybdate appears when the solution is titrated.

TABLE II.—RESULTS FOR THE DETERMINATION OF COPPER IN ALLOYS, ETC.

Sample	Copper found by electroanalysis, %	Copper found by the present method, %	Number of analyses	Standard deviation relative, %
Brass[a]	60·40	60·51	17	0·34
Copper alloy[b]	78·39	78·52	6	0·22
Copper concentrate	11·96	12·17	9	0·73
Bornite	44·70	44·50	4	0·94

[a] The alloy contains also 38·65% of zinc and 0·92% of lead.
[b] The alloy contains also 3·80% of tin, 4·65% of lead and 6·57% of zinc.

DISCUSSION

Existing complexometric methods have not solved the problem of determining copper^{II} in the presence of more than one or two foreign ions. The present method achieves this by making use of a selective reduction of copper^{II} in the copper^{II}-EDTA complex to copper^{I}, whereupon an equivalent quantity of EDTA is liberated. The ions most commonly encountered, over a wide range of concentrations, do not interfere with the determination. Interfering ions (*i.e.* cadmium^{II}, mercury^{I}, mercury^{II}, *etc.*) are not usually met in copper alloys and concentrates. The method is rapid and especially convenient for the determination of copper in materials rich in copper.

Zusammenfassung—Die Methode beruht auf die Tatsache, daß Cu(II) stabile Komplexe mit ÄDTE bildet, wobei Cu(I) von der ÄDTE nicht gebunden wird. Bei einer Reduktion von komplexgebundenem Cu(II) zu Cu(I) wird aus diesem Grunde eine äquivalente Menge ÄDTE freigesetzt. Die Versuchslösung wird mit einem Überschuß von Na_2ÄDTE versetzt, auf pH 5,5–6 korrigiert und mit $Pb(NO_3)_2$-Lösung in Gegenwart von Xylenolorange zurücktitriert. Alle Ionen (einschließlich Cu(II)), die stabile Komplexe mit ÄDTE bilden, werden auf diese Weise Komplex gebunden. Jetzt wird die Lösung angesäuert, das frei gewordene Cu(II) mit Thiokarbamid zu Cu(I) reduziert, wieder auf pH 5,5–6 neutralisiert und die freigesetzte ÄDTE mit 0,025 m $Pb(NO_3)_2$ weitertitriert. Die Ionen, die sehr oft das Kupfer begleiten (Ag(I), Pb(II), Zn(II), Ni(II), Bi(III), Sb(III), As(III), Fe(III), Al(III), Sn(IV) u.a.) stören bei der Bestimmung des Kupfers nach dieser Methode nicht. Der Einfluß anderer Ionen wurde auch untersucht. Die Methode wurde bei der Bestimmung des Kupfers in Kupferlegierungen, Kupferkonzentraten und Kupfermineralien mit Erfolg angewendet.

Résumé—La méthode est basée sur le fait que Cu^{II} donne de complexes stables avec l'EDTA, par contre de Cu^{I} qui ne forme pas de complexes de la sorte. On réduit le Cu^{II} à Cu^{I} de manière qu'on délibère une quantité équivalente d'EDTA. A la solution qui contient Cu^{II} et d'autres ions, on ajoute un excès de Na_2EDTA, après quoi on ajuste le pH à 5,5–6 et on titre avec une solution de $Pb(NO_3)_2$ en présence de xylenol orange. De cette façon, tous les ions formant chez ce pH des complexes stables avec EDTA sont liés. On accomplit la reduction de Cu^{II} à Cu^{I} à l'aide de thiourea dans un milieu fort acide, où les complexes de Cu^{II} avec EDTA sont dissociés. On amène le pH de la solution à 5,5–6 et on titre avec 0,025 m $Pb(NO_3)_2$ la quantité libérée d'EDTA. La détermination peut être accomplie en présence des ions qui d'habitude accompagnent le cuivre. L'influence des autres ions a aussi été étudiée. En appliquant cette méthode, nous avons fait des dosages de cuivre dans les alliages de cuivre, les concentrates et différents minéraux.

REFERENCES

[1] G. Schwarzenbach and E. Freitag, *Helv. Chim. Acta*, 1951, **34,** 1503.
[2] S. J. Feinberg, *Zavodskaya. Lab.*, 1958, **24,** 534.
[3] O. B. Budevsky, *ibid.*, 1958, **24,** 535.
[4] K. L. Cheng, *Analyt. Chem.*, 1958, **30,** 243.
[5] B. Singh, S. Sahota and A. Narang, *Z. analyt. Chem.*, 1961, **182,** 241.
[6] G. Martens and K. Schwarz, *ibid.*, 1957, **159,** 22.
[7] R. Přibil and V. Veselý, *Talanta*, 1961, **8,** 743.
[8] G. Lystsova, *Zavodskaya Lab.*, 1961, **27,** 964.
[9] J. Kŏrbl, R. Přibil and A. Emr, *Chem. Listy*, 1956, **50,** 1440.

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SEPARATION OF CERTAIN CATIONS FROM MIXTURES OF VARIOUS CATIONS ON ION-EXCHANGE PAPERS—I

SILVER AND THALLIUM

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Summary—Development with solutions providing selective complexation and pH control permits the complete separation of silver or thallium ions from multicomponent mixtures of various ions on ion-exchange papers. Complete recovery as well as separation is demonstrated for silver on columns of ion-exchange resin.

ONE of the important uses of ion exchange is for the separation of cations from anions.[1] In this report, solvents which selectively cause one cation to remain positively charged while all other cations are anionically complexed are used in conjunction with filter paper impregnated with anion-exchange resins to provide a complete separation of that one cation from a complex mixture. As the solvent flows, the cation migrates rapidly while the anions undergo ion exchange and migrate slowly or not at all.

Differential migration in an ammonical solution of oxalate plus cyanide permits the separation of thallium[I] ions from univalent silver and mercury ions and from various multivalent cations. Differential migration in an ammoniacal solution of ammonia-triacetic acid (nitrilotriacetic acid) permits the separation of silver from univalent thallium and mercury ions and from various multivalent cations.

Separate studies with silver ions show that the qualitative separation procedures developed on ion-exchange papers can be rendered accurately quantitative by use of columns of ion-exchange resin. As has been reported for other ion-exchange procedures,[2] the results of ion exchange on papers and in columns of the same resin are entirely analogous.

EXPERIMENTAL

Studies on ion-exchange papers

Migration apparatus. Paper chromatograms were developed by the downward flow of solvent in a bench-top Chromatocab (Research Specialties Co., Model C-350). Amberlite SB-2 ion-exchange papers (batch No. 7804) were used in sheets 18 in. long (except in one experiment) by up to 10 in. wide, exactly as supplied (Rohm and Haas Co.). This paper contains about 45% by weight of Amberlite IRA-400 strong-base anion-exchange resin in the chloride form. Migrations were performed perpendicular to the machine direction of the paper.

Samples were applied to the dry paper at marked locations by means of a micropipette. The origin was close to the developer and always the same distance from the surface of the developer. A migration distance of about 40 cm was available between the origin and the bottom of the sheet. The spots were dried for 15 min after application by hanging the paper in a hood and using a hair dryer. The paper was placed in the chamber, with the end closest to the origin line in a solvent trough, and allowed to equilibrate for 45 min in the presence of a container of developer. The developer was then introduced into the trough through a hole in the top of the cabinet, and development was allowed to proceed until the solvent front was close to the bottom of the paper; this required about 3 hr with the solutions used. The paper was then removed from the chamber, and the solvent front was marked; the paper was dried for 30 min and sprayed with the proper reagents to make the zones of the substances visible.

Developing solvents. Three solvents were used to develop the chromatograms in this work. To separate silver, 0·0125*M* ammonia-triacetic acid in 3·0*M* ammonia, pH 11·0, was used. For studies involving thallium (1) 0·05*M* potassium cyanide and 0·05*M* ammonium oxalate in 0·185*M* ammonia, pH 9·5, and (2) 0·05*M* potassium cyanide and 0·075*M* ammonium oxalate in 0·20*M* ammonia were employed. These solvents were chosen because electrochromatographic studies[3] had indicated that they would give the desired separations and would not interfere with detection tests.

Initial zones. To compare the migrations of various cations (listed below) in the systems chosen, single spots [10 μl for all ions except Ni (20 μl), and Al, Sb, and Sn^{IV} (25 μl)] were developed at a concentration of 0·05*M*. The amount of sample was chosen so that the zone could be detected after migration and concomitant dilution.

Sample solutions were prepared by dissolving the proper amount of reagent-grade nitrate, chloride, or acetate. Antimony and arsenic chloride, mercurous nitrate, and cerium ammonium sulphate solutions were stabilised with acid.

Synthetic mixtures of ions were tested to ascertain whether there was any variance in behaviour from the single cation solutions to the mixture. A mixture of all cations studied could not be used because of the incompatibility of some of the ions. A representative compatible mixture contained Ag, Cd, Co, Cu, Fe, Pb, Ni, Tl, Al, Ce, Mg, Zn, Cr, Mn, and Ba. The concentration of each ion was 0·05*M* except that nickel was 0·10*M* and aluminium was 0·15*M*.

Detection of zones. Four spray reagents were sufficient to detect all ions studied. All the ions which reacted with a given reagent were run on one piece of paper, which was then treated with this reagent. Likewise, when a synthetic mixture was separated, four spots of mixture were run under identical conditions on four separate pieces of paper, which were sprayed with the four reagents so as to account for every ion.

Many ions were converted to coloured sulphides by spraying the paper with a 2% solution of yellow ammonium sulphide. These included Ag, Tl, Pb, Cu, Cd, Fe^{III}, Co, Ni, Sb, Hg^{I}, Hg^{II}, As, and Sn^{IV}. Some of these ions formed coloured zones when spotted on the dry ion-exchange paper and required no spray for detection. For nickel with the ammonia-triacetic acid solvent and copper with the oxalate solvents, no sulphides formed upon spraying with the reagent. For these cases, it was necessary to spray the paper with 3·0*M* hydrochloric acid and allow it to stand several hr before spraying with sulphide.

Al, Ce^{IV}, Mg, and Zn were detected by spraying with 8-quinolinol (0·5 g in 60 ml of absolute ethanol, diluted to 100 ml with water), and viewing the resultant fluorescent spots in a darkened room under ultraviolet light.

Mn^{II} and Cr^{III} were located with alkaline ammoniacal silver nitrate (0·1*M* silver nitrate in 2*M* ammonia, mixed with an equal volume of 6*M* sodium hydroxide).

Barium ions were located by spraying with 3*M* acetic acid followed by a freshly prepared 0·1% solution of potassium rhodizonate.

Studies on columns of ion-exchange resin

Ion-exchange resin. Amberlite CG-400 (lot No. SW-3203), strong-base anion-exchange resin, 200-400 mesh, in the chloride form, was used (Rohm and Haas Co.). The resin was treated before use by the recommended procedure.[1]

Ion-exchange column. In all experiments, columns of resin 10 cm high were used. They were prepared by pouring a slurry of resin and eluent into columns, 15 cm × 3·90 cm^2 (Ace Glass Co., drawing T-3422). A glass-paper disc was placed on top of the bed of resin to prevent its disturbance as solutions were added.

Exploratory studies. The separation of silver was studied on ion-exchange columns in order to compare the results with those obtained on ion-exchange papers, and to indicate the quantitative usefulness of the systems studied. The only eluent employed was the ammoniacal ammonia-triacetic acid solvent described above.

A series of solutions, each 0·1*M* in silver and 0·1*M* in one of the ions listed in the mixture above, was eluted in turn through a column of resin. Five ml of solution were mixed with eluent, loaded on to the column with a pipette, and washed into the bed with several portions of eluent. A separatory funnel containing a supply of eluent was attached to the column with a rubber stopper. The flow rate of eluent was regulated at 1–2 ml per min. Effluent was automatically collected from the point of sample addition in constant fractions of about 5·0 ml.[4] Each fraction were tested qualitatively for silver and the other metal ion in the pair. The elution was stopped when all the silver had been eluted from the column.

To test qualitatively for the presence of each metal, common spot tests were used, such as hydrochloric acid (after neutralisation with HNO_3) for Ag; sulphide for Cd, Co, Cu, Fe, Pb, and Tl; Eriochrome Black T (purple colour) for Al, Mg, Mn; potassium rhodizonate (brown precipitate) for Ba; dithizone in CCl_4 for Ni and Zn; and Xylenol Orange (pH 4·5-red) for Cr.

Later, a series of elutions of the fifteen-component mixture above was run. The solution used was a standard solution of 0·09943*M* silver nitrate which was also 0·025*M* in each other ion. Exactly 5 ml of this mixture, mixed with eluent, were added to the column and all the silver was collected in a single effluent fraction. To check the recovery of the silver, it was determined gravimetrically by neutralising the ammonia with about 40 ml of 0·15*M* nitric acid, precipitating silver chloride with a carefully controlled excess of 0·12*M* hydrochloric acid, and continuing as usual.[5] The ammonia-triacetic acid in the eluent did not at all interfere with this determination.

RESULTS

Separation of silver ions from thallium and multivalent cations in ammoniacal ammonia-triacetic acid on ion-exchange papers

In the interpretation of results, use is made of the familiar equation

$$R_F = \frac{\text{distance travelled by leading edge of solute zone}}{\text{distance travelled by solvent front}} \qquad (1)$$

Ammonia-triacetic acid forms anionic chelate complexes with multivalent cations and silver and thallium^{I} ions. In strongly ammoniacal ammonia-triacetic acid, however, the silver becomes cationic, forming $Ag(NH_3)_2^+$, while thallium^{I} and multivalent ions remain anionic. This has been proven by electrochromatographic studies, by noting the direction of migration of various ions in background solutions of this nature.[3]

Development with this solvent on anion-exchange paper causes silver to move with a mean R_F value of 0·77. Of all other ions tested, only thallium shows appreciable movement ($R_F = 0·21$); copper has $R_F = 0·092$ and cadmium has $R_F = 0·070$. No other ion leaves the origin. The significant movement of thallium indicates that ammonia-triacetic acid complexes multivalent ions much more strongly than it does univalent thallium. Univalent mercury is unstable in ammoniacal solutions, decomposing to mercury and mercury^{II} ions, neither of which leaves the origin.

When developed over the full 40 cm of paper afforded in the present apparatus, the rear of the silver zone is separated from the front of the thallium zone by 17·5 cm. The silver zone has an average length of 2·7 cm and an average width of 1·0 cm after development.

In the course of this study, 12 migrations of silver, both from single spots and from mixtures, were performed. The standard deviation of the resultant R_F values was $\pm 0·03$ R_F unit.

Because thallium is the only other ion with significant movement in the system used, studies to determine how quickly silver could be separated from the other ions were made using only thallium and silver ions. The separation was considered complete when the rear of the silver zone was separated from the front of the thallium zone by one cm. It was found that on a sheet of paper 14 in. long and 6 in. wide, this requirement was met in 15 min. During this short period of time the solvent front moved about 4·5 cm past the origin, which was more than expected from the results of the usual 3-hr migrations. This indicates that the rate of downward flow of solvent substantially decreases with time, an effect noted in other studies.[6] As was expected, the silver zone measured only 1·2 cm after this short period of migration, compared with the greater tailing (above) during the usual 3-hr migrations.

These results indicate that by development for only 15 min in the system described silver can be completely separated from all ions studied. The procedure can be

further shortened by omitting the pre-equilibration of the paper (which is often omitted when one-phase solvents are employed) and omitting the drying of the paper before spraying with the developing reagents.

Separation of thallium ions from silver and multivalent cations in ammoniacal oxalate plus cyanide on ion-exchange papers

Electrochromatography[3] has proved that all multivalent cations and silver ions are converted into complexes in the presence of oxalate and cyanide ions, while thallium ions remain as cations. These are separable by ion exchange. Univalent mercury again is unstable in the presence of ammoniacal cyanide, forming mercury and mercury^{II} ions.

Of the two ammoniacal oxalate-cyanide developing solvents which were studied in the attempt to find a solution which would facilitate the separation of thallium from the other ions, solvent (2) (above) proved the more successful. In it, thallium migrated with an $R_F = 0{\cdot}30 \pm 0{\cdot}02$ (standard deviation, 7 trials), while no other cation, except magnesium, showed movement from the origin. The thallium zone had an average length of 5·3 cm after the usual 3-hr development period, which means that the rear of the zone was 7·3 cm from the origin.

With solvent (2), the magnesium zone moves with an average value of $R_F = 0{\cdot}20$ having a zone length of 3–4 cm after a 3-hr development period. Results of several trials indicate that under the conditions used, an average thallium zone would separate completely from an average magnesium zone by about 0·75 cm, but that the separation was not complete every time. The separation of thallium from all other ions tested ($R_F = 0$) is easily accomplished.

Solvent (1) contained a lower concentration of oxalate ions and ammonia than solvent (2). When solvent (1) was used as the developing solvent, thallium moved more slowly with less tailing [$R_F = 0{\cdot}30 \pm 0{\cdot}01$ (standard deviation, 6 trials); average length = 5·3 cm; rear of zone moved 5·1 cm from the origin] than in solvent (2). Magnesium also moved more slowly, the rear of its zone barely leaving the origin. With solvent (1) however, the ions studied, when applied to the paper separately, did not behave in the same way as they did when applied as part of the mixture. Some of the ions showed movement from the initial zone of mixture, but not when present as a single component. This indicated that there was too low a concentration of complexing agent in solvent (1); results for a given ion with solvent (2) were the same whether that ion was alone or part of a mixture.

The significant movement of the magnesium zone in the two solvents which were used indicates that the magnesium ions are either in the form of weak anionic oxalate complexes, or un-ionised covalent oxalate complexes[7] (or both), and therefore do not undergo ion-exchange reactions with the resin in the paper to the same extent as do the other multivalent ions.

These studies show that thallium can be completely separated from all ions studied, except perhaps magnesium ions, by development as directed above.

Separation and analysis of silver ions in ammoniacal ammonia-triacetic acid on columns of ion-exchange resin

As well as being used to separate silver or thallium, the techniques described above can be used to determine these ions quantitatively by resorting to the usual methods for

determining the amount of material in a spot of a developed paper chromatogram. These methods include cutting-out the spot followed by elution of the material and analysis, or relating the area of the spot to the amount of material present. The most accurate method of making these separation techniques quantitative, at least for macro amounts of silver and thallium, was to perform the separations in the same way, but on columns of that ion-exchange resin which was contained in the papers. Results for the two systems were found to be entirely analogous.

Elutions of samples containing silver and each metal of the mixture in turn proved that no metal appeared in the effluent before all the silver had emerged. In many cases the metals formed a coloured band when sorbed on top of the bed; this was found not to move significantly on elution with the ammoniacal ammonia-triacetic acid eluent. In all cases, qualitative analysis of the effluent proved the absence of any ion except silver. The break-through volume for silver was 25 ml, and the elution was complete by the time 45 ml of effluent had been collected. The break-through volume for thallium, the only other ion to show movement on the ion-exchange papers, was found to be greater than 200 ml.

Elutions of the standard solution of silver in admixture with the other ions proved that the silver was eluted between the same volumes of effluent as above. Gravimetric analysis of the effluent for silver ion showed an average recovery (6 trials; standard deviation = 0·40%) of 71·1 mg of silver chloride compared to a theoretical value of 71·2 mg for a mean error of −0·1 mg and a relative mean error of −0·14%.

These results prove that silver can be completely separated and recovered from mixtures containing any or all of the ions studied. Because analogous results were obtained with silver on columns and on paper containing the same ion-exchange resin, the thallium separations can undoubtedly be made quantitative on columns of chloride-form anion-exchange resin.

DISCUSSION

This paper is the first in a series in which certain ions are separated by ion exchange from multicomponent mixtures of various ions because of the selective complexing of the developing solvent. Within Strain's definition,[8] the separations are chromatographic in nature, because they are based upon selective differential migration of the ionic complexes formed.

The experiments were performed with cations representative of many elements of the Periodic Table. Therefore, it should be possible to separate silver or thallium from almost all cations except those of the alkali metals, which are not anionacally complexed by any known reagent.

Zusammenfassung—Entwicklung mit Lösungen, die selektive Komplexformer enthalten, sowie pH-Kontrolle gestatten die vollständige Trennung von Silber oder Thallium von Mehrkomponentensystemen mittels Ionenaustauscherpapieren.

Vollständige Trennung und Wiedergewinnung von Silber mittels Ionenaustauschersäulen wird demonstriert.

Résumé—Sur papier échangeur d'ions, le développement par des solutions qui conduisent à une formation sélective de complexes et à un contrôle du pH permet la séparation complète des ions argent ou thallium de mélanges de différents ions. La récupération complète, ainsi que la séparation, sont montrées, dans le cas de l'argent, sur des colonnes de résine échangeur d'ions.

REFERENCES

[1] Wm. Rieman III and A. C. Breyer, *Columnar Liquid-Solid Ion-Exchange Processes*; Chapter 35, Part I, Vol. 3 of *Treatise on Analytical Chemistry*, edited by I. M. Kolthoff and P. J. Elving. Interscience Publisher, New York, U.S.A., 1961.
[2] D. K. Hale, *Chem. and Ind.*, 1955, 1147.
[3] H. H. Strain, J. F. Binder, G. H. Evans, H. D. Frame, Jr. and J. J. Hines, *Analyt. Chem.*, 1961, **33**, 527.
[4] J. Beukenkamp, S. Lindenbaum, and Wm. Rieman III, *ibid.*, 1954, **26**, 505.
[5] W. J. Blaedel and V. W. Meloche, *Elementary Quantitative Analysis*. Row, Peterson and Company, White Plains, N.Y., U.S.A., 1957, p. 643.
[6] S. E. Wood and H. H. Strain, *Analyt. Chem.*, 1954, **26**, 260.
[7] K. J. Pederson, *Trans. Faraday Soc.*, 1939, **35**, 276
[8] H. H. Strain, *Analyt. Chem.*, 1958, **30**, 620.

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DETERMINATION OF MAJOR AND MINOR ALKALIES IN SILICATES BY DIFFERENTIAL FLAME SPECTROPHOTOMETRY*

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Summary—By attaching an external galvanometer circuit to a Beckman DU spectrophotometer and making use of an improved and highly stable air-natural gas flame, it is possible to apply the principle of differential measurement to the flame spectrophotometric determination of the major and minor alkalies and alkaline earths. Although it is doubtful that any reasonably rapid, purely flame photometric, method can ever equal the best flame-supported gravimetric techniques in determinations of major alkali constituents, procedures have been worked out whereby rubidium and caesium can be determined with improved precision, and the accuracy of sodium and potassium determinations is significantly increased.

INTRODUCTION

IN 1955, Ellestad and Horstman[3] described an air-natural gas flame attachment for use with a spectrophotometer in the determination of lithium. In 1956, Horstman[6] used the same apparatus for rubidium and caesium as well as for lithium, and a later paper[7] reported a large number of determinations of these elements in igneous and sedimentary rocks.

Horstman estimates an accuracy of 5 ppm of caesium and 10 ppm of rubidium for his determinations in the range 10–200 ppm, and 5–10% of the amount present with larger amounts.

By modifying the apparatus and the chemical techniques, the limit of detection for rubidium and caesium has been extended to about 2 ppm of Rb_2O and 1 ppm of Cs_2O in the sample, and by differential measurement, precision in the determination of both the major and the minor alkalies has been considerably improved.

Separate samples are required for sodium and potassium, for rubidium and caesium, and for lithium. In the preparation of sample solutions, a variation of the method of Abbey and Maxwell[1] is used in preference to the longer procedure of Horstman; however, lithium is not completely recovered in this procedure, and for its accurate determination the method of Ellestad and Horstman[3] is recommended, with some slight refinements. The Ellestad-Horstman procedure for lithium cannot be used for the other alkalies.

Rubidium and caesium emission in the flame is greatly enhanced by potassium, and if this enhancement is to be used to advantage, the potassium content of the sample solutions must be controlled. Perhaps the simplest way to do this is to add potassium to the sample up to a standard concentration, and this expedient is here

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adopted. Because the potassium content of the sample must be accurately known, the determination of this element must be made a part of any flame photometric method for the determination of rubidium and caesium.

Horstman preferred to make standard solutions to correspond to each unknown. This requires, in effect, a recalibration for each sample, but nevertheless may be an advantageous procedure, especially for samples of widely varying potassium content.

It is difficult to obtain potassium salts completely free from rubidium, so that the rubidium content of the potassium salt used as an additive and as a standard must be determined, and suitable corrections made.

The sensitive rubidium lines available for flame photometry are those of wavelength 780·02 mμ and 794·76 mμ. These are unfortunately so close to the potassium lines 766·49 and 769·90 mμ that the Beckman DU monochromator resolves the two elements only imperfectly. Despite the proximity of Rb 780 to K 770, this line was chosen after many experiments in preference to the Rb 795 used by Horstman, largely because reproducibility is slightly better at this wavelength. Actually, there is little to choose between the two; the greater potassium interference at Rb 780 is compensated for by the lower sensitivity at Rb 795.

The 852·11 line is used for the measurement of caesium. Although there is no direct potassium interference at this wavelength, the flame background is relatively high, and thus an absolutely steady and reproducible flame is as necessary with caesium as with rubidium.

The determination of sodium and potassium is only slightly affected by the small amounts of lithium, rubidium and caesium normally found in silicates. Provision is made in the procedure to correct for the inter-effects of potassium and rubidium.

While lithium is best determined on a separate sample, an approximate preliminary figure may be obtained on the solutions used for the other alkalies.

EXPERIMENTAL

Apparatus

Changes in the original design of the flame attachment described by Ellestad and Horstman[3] improve stability, and make practicable the use of a more sensitive indicating ammeter than that provided in the Beckman DU spectrophotometer; an external galvanometer circuit, specifically that of a Coleman Universal spectrophotometer, is used. Presumably, a 'Galv-o-meter' or similar instrument—or a recording device—would serve as well.

Sensitivity is increased by the use of an additional 1·5-V dry battery in the Coleman instrument, increasing available voltage to 3·0. The phototube is the red-sensitive caesium oxide tube normally used for flame photometry with the Beckman DU spectrophotometer.

To attach the external galvanometer, a telephone plug is mounted in the base of the DU spectrophotometer and wired across the indicating ammeter. A lead from this plug through a 100,000-Ω variable resistance carries a controlled portion of the current from the DU spectrophotometer to the galvanometer plug of the Coleman instrument. The resistance box also contains a reversing switch and an additional series-connected 100,000-Ω resistor which may be switched in and out of the circuit at will.

As in the original apparatus, the burner is mounted in a cylindrical mirror of polished aluminium sheet. The mirror is enclosed in a brass tube, from which a light-pipe of polished aluminum projects to within about 2 cm of the entrance tunnel of the DU spectrophotometer. This device increases the radiation striking the instrument mirror by about 20%. The burner and chimney are mounted on movable supports so that the optimum portion of the flame may be sampled. It would seem advantageous to mount the spectrophotometer in such a way that the slit is horizontal instead of vertical, but this has not yet been investigated.

Natural gas is supplied to the spray chamber itself, rather than to a mixer in the spray tube leading from it, and enters through an inverted funnel, which increases turbulence and protects the water seal at the bottom of the chamber. The spray tube is extended into the chamber to increase mixing

efficiency. A second trap at the bottom of the burner compartment requires a small addition of water from time to time.

The aspirator itself is identical to that used by Ellestad and Horstman.[3] Air pressure at the atomiser is about 70 cm of mercury, and gas flow is roughly adjusted to the maximum at which no peaking of the flame occurs. A final adjustment of gas flow should be made to give maximum instrument response for each element at the time of measurement. Undoubtedly air pressure will have to be changed to suit gas composition. Air pressure and gas flow must be held constant within very close limits; this is easily done by placing two or more pressure and flow regulators in series on the air and gas lines. The flame attachment is illustrated in Fig. 1.

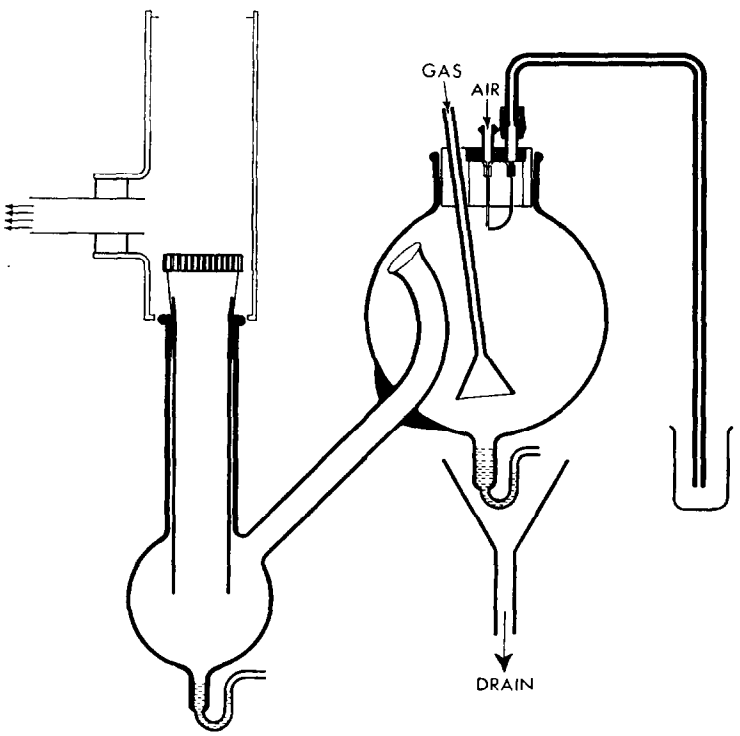


FIG. 1—Flame Attachment. The atomiser consists of two hypodermic needles mounted in a brass plug in the rubber stopper closing the spray chamber. Air enters through a No. 15 needle, and the test solution through a No. 21 needle. The arrangement is similar to that suggested by Barnes *et al.*[2] The spray chamber is made from a 2-litre round flask, and the burner chamber from a 250-ml flask with a special neck to accept the Meker burner cap. The burner tube is installed by grinding off the flange which holds the burner grid and removing the latter. Best results are obtained if the grid is returned to the burner cap without reflanging. The capillary through which solution is drawn into the spray chamber should be selected to give a flow rate of about 2–3 ml per min. A capillary bore of 0·5 to 0·6 mm is satisfactory.

Features which are of particular importance in the determination of trace alkalies are the almost perfect stability and reproducibility of the flame, and the minimum of maintenance required. As long as solutions are free from foreign solids, the burner and atomiser will operate for weeks without need for cleaning or attention of any kind, even when solutions containing several g/litre of salts are routinely passed through it. The memory of the flame is surprisingly short; distilled water will completely remove all traces of a sodium flame in about 30 sec after aspirating a solution containing 10,000 ppm of Na_2O. If salts become deposited on the burner grid, they may be removed simply with a jet of water, without dismantling the apparatus.

It is possible that even greater sensitivity might be attained with a red-sensitive photomultiplier tube instead of the arrangement described; however, the controlling factor is the steadiness and reproducibility of the flame background, rather than the sensitivity of the detector. This is particularly

true in the case of rubidium, for this element nearly always is associated with much larger amounts of potassium, so that in practice it must always be measured over a large potassium background. Even if a monochromator which completely resolves the two elements is available, the enhancement effect must still be quantitatively dealt with, and control of this effect likewise requires a completely steady flame.

Attempts to use the Beckman flame attachment with oxygen and acetylene in a similar procedure to that described were not successful.

Reagents

Standard alkali solutions: Neutral alkali sulphate solutions to be used as standards should be prepared from the purest salts available.

Mix the salt thoroughly, and weigh 0·1 to 0·2 g into a weighed 55-ml flat-bottom platinum dish. Add a little water and about 1 ml of 1:1 sulphuric acid, and evaporate to dryness. Increase the temperature until excess acid is removed, and hold the dish and contents at the highest plate temperature for some time to remove bisulphate. Heat cautiously with a small flame, then at the full heat of a good Meker burner for 1 min. Weigh, and repeat the ignition to constant weight.

On the basis of the assay, weigh enough of the salt to give a solution of the desired concentration, dissolve in somewhat less than the required volume of water, and heat the solution to 95–100° for a few hr to destroy organisms which otherwise precipitate after standing. Dilute to volume with boiled water, and filter into Pyrex bottles which have been thoroughly cleaned and dried.

Solutions containing 10,000 or 20,000 ppm of Na_2O and K_2O, and 1000 ppm of the other alkalies are convenient, and may be diluted as needed.

All solutions should be examined for foreign alkalies and alkaline earths on the flame photometer. Determination of rubidium in the standard potassium solution is a matter of some difficulty, because of interference and enhancement effects. A satisfactory procedure is as follows:

By dilution of stock solutions, prepare a series of solutions with 1000 ppm of K_2O, 1000 ppm of MgO, and increasing amounts of Rb_2O in increments of 0·2 or 0·5 ppm, up to 2·0 ppm. At the rubidium wavelength setting near 780 mμ (established as accurately as possible with a pure rubidium solution, not a potassium-rubidium solution) and a slit of 0·14 mm, set the Beckman and Coleman controls so that the galvanometer index on the latter instrument reads at one end of the scale with 2·0 ppm of Rb_2O, and at the other end with no rubidium added. Read each of the intermediate solutions directly from the galvanometer scale, adjusting the dark current to zero between readings. Plot galvanometer readings against ppm of Rb_2O. Extrapolate the straight portion of the curve (or rather, draw a straight line asymptotic to it) to meet the ordinate at a point representing a negative Rb_2O content (Fig. 2). This gives a preliminary estimate of the rubidium content of the potassium solution. Repeat the procedure, adjusting the instrument settings so as to take the estimated rubidium impurity into account, and again plot the results, Repeat, changing settings as necessary, until a straight line between 0 and 100 on the galvanometer scale is obtained. Once the T scale reading on the DU spectrophotometer has been established for zero Rb_2O, there is no further difficulty in determining the absolute rubidium content of any solution containing 1000 ppm of K_2O and 1000 ppm of MgO.

Because of uncertainties in this procedure (for instance, it is assumed that a straight line relationship exists down to the limit of detection), it seemed desirable to check results by independent methods, *viz.*, emission spectrography and also isotope-dilution mass spectrometry. Fair agreement between methods was obtained with samples of potassium salts (both 'Spec-pure') containing 20 and 40 ppm of rubidium.

Preparation of sample solutions

Weigh 0·5000 g (for rubidium and caesium) and 0·0500 g (for sodium and potassium) of the suitably prepared sample into 55-ml platinum dishes. Other sample weights may, of course, be used. Add a little water and 1 ml of 1:1 nitric acid, and warm gently to remove carbonate, keeping the dish covered. Wash down and add 1 ml of 1:1 sulphuric acid and 5–15 ml of hydrofluoric acid, then evaporate slowly, increasing the plate temperature gradually until fumes of sulphuric acid appear. Cool, dilute with water, and warm gently until soluble salts are in solution. If sample attack is incomplete, repeat the hydrofluoric acid treatment and again evaporate to fumes and dilute. Repeat until a clear solution is obtained. Two or three evaporations without hydrofluoric acid addition may be required to remove fluoride.

Add 2 ml of a magnesium sulphate solution containing 25 mg of MgO per ml, or, if the magnesium content of the sample is known, add just enough to make a total of 50 mg of magnesium oxide. Evaporate to fumes, and gradually increase the plate temperature until excess acid has been removed. Continue heating at the maximum plate temperature for 2–4 hr to decompose bisulphate. Transfer the dish to a platinum triangle, and heat first with a small flame, then finally for 1 min at the full heat of a good Meker burner.

Cool the residue, add 15–25 ml of water, and digest on the steam bath for 30 min or more. Up to this point the 50-and 500-mg samples are treated similarly.

Evaporate the suspension of the 50-mg sample to about 5 ml, and filter into a 50-ml volumetric flask through a 5·5-cm Whatman No. 44 paper. Wash thoroughly with hot water.

Filter the suspension of the 500-mg sample into a 150-ml beaker, breaking up the flakes of oxide with a rubber-tipped rod. Wash very thoroughly with hot water to a volume of 100 ml or more. Add about 50 mg of pure calcium carbonate to the filtrate, and evaporate to small volume on the steam bath. In this process, any traces of free acid remaining after the ignition are neutralised, and the final

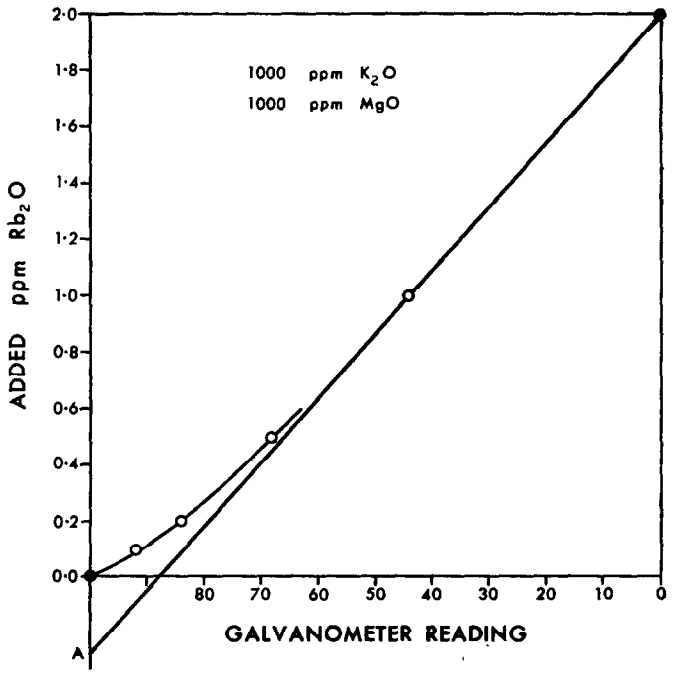


FIG. 2.—Extrapolation method of determining contamination of the standard potassium solution. A similar procedure may be followed for any alkali or alkaline earth trace constituent in strong stock solutions. The distance OA gives a first approximation to the concentration of the contaminant.

solution should have a pH close to 6. The precipitate of hydrous oxides formed as a result of the neutralisation should be small. If a large precipitate forms, heating over the Meker burner was inadequate. With the 50-mg sample, there should be no difficulty in obtaining a neutral solution without the additional step.

When the volume of the solution has been reduced to about 10 ml, filter through a small Whatman No. 44 paper into a 50-ml volumetric flask, and wash thoroughly with hot water, leaving enough room in the flask for later addition of standard alkali solutions. In some cases, where very little rubidium or caesium is expected, it is advantageous to use a 25 ml flask. The magnesium addition earlier in the procedure should then be halved.

The pH of all final solutions should be very close to 6·0, and it is most advisable to check this. Unless sodium is to be determined, the check is easily made by dropping a small piece of nitrazine paper into the solution just before filtration, and observing the colour it assumes. Nitrazine is an ideal indicator for the purpose.

For the determination of lithium, weigh 0·1 to 0·5 g of the sample into a platinum dish, and treat exactly as above, up to the point where heating has been continued for 2–4 hr to remove bisulphate. Wash the residue into a 150-ml beaker, dilute to about 100 ml, heat to boiling, and add to the boiling solution small portions of basic lead carbonate until it is no longer acid to methyl red. Filter at once into another beaker, and wash thoroughly with hot water. Add about 50 mg of basic lead carbonate to the filtrate, and evaporate to 10–15 ml on the steam bath. *Do not evaporate to dryness.* Filter while still hot into a 50-ml volumetric flask and wash the residue thoroughly with hot water, leaving room in the flask to accept later addition of standard sodium solution.

Flame photometric procedure

Determination of sodium and potassium: Dilute the solution of the 50-mg sample to 50 ml and mix. For potassium, adjust the wavelength setting to give maximum response at about 766 mμ, and the sensitivity control to give 100 × ·1 T reading with a neutral sulphate solution containing 100 ppm of K_2O and 1000 ppm of MgO, using a 0·05-mm slit. Obtain a preliminary value for the unknown from a calibration curve prepared from standards with 100, 92, 84, *etc.*, ppm of K_2O. Magnesium has a depressing effect on the potassium emission, so it is important that all readings be made with very nearly the same concentration of magnesium ion in solution (Fig. 3). To help control the effect of rubidium in the unknown, all readings must be made at the same slit setting.

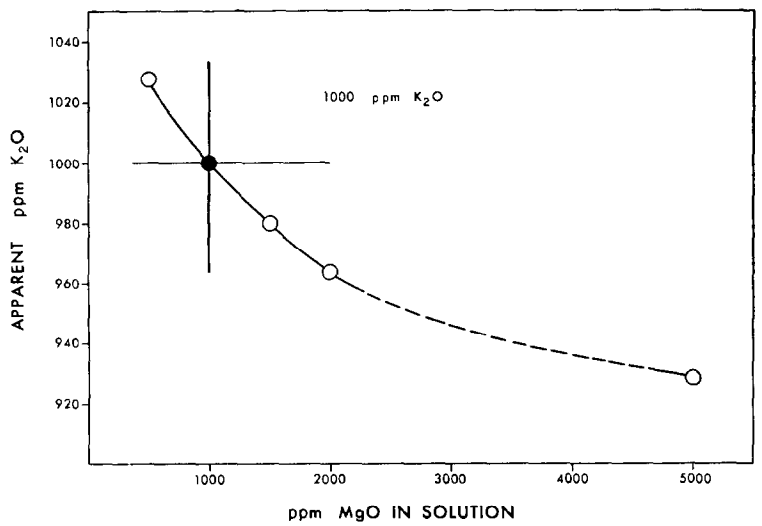


FIG. 3—Effect of magnesium on potassium emission. Instrument settings are made so that a solution with 1000 ppm of K_2O and 1000 ppm of MgO gives a reading of 100 × ·1 on the Beckman T scale. The graph shows the variation in apparent potassium content with change in the concentration of magnesium.

Make a preliminary sodium reading in the same way, using a wavelength near 589 mμ. Use of the external galvanometer is not necessary for these preliminary readings.

Obtain accurate values by setting the instrument controls using solutions with slightly less or slightly more Na_2O and K_2O than the unknown, and measuring the difference with the external galvanometer. Standards containing both sodium and potassium in appropriate concentration, as well as magnesium, should be prepared for each sample. Galvanometer sensitivity is conveniently adjusted so that the full scale represents 20 ppm of Na_2O or K_2O in solution. A separate calibration curve should be prepared for each 20-ppm range, because the relation between galvanometer reading and alkali content is not exactly linear.

Preliminary readings on the 50-mg sample may be made for lithium, rubidium and caesium, but there is seldom sufficient of these elements to make it worthwhile. Lithium values thus obtained are very approximate.

Reserve the solution for a final potassium reading to be made after the rubidium and caesium determinations are completed.

On the basis of the potassium determination, add to the solution of the 500-mg sample enough standard potassium sulphate solution to bring its concentration up to 1000 ppm of K_2O after dilution. Dilute to 50 ml and mix. Other standard potassium concentrations may be used; however, below about 500 ppm the K_2O concentration becomes increasingly critical, and above 2000 ppm flame stability is adversely affected.

Determination of rubidium: Using a pure rubidium sulphate solution (containing no potassium), adjust the wavelength setting near 780 mμ to give a maximum response, using a 0·14-mm slit. The external galvanometer should be used in making this setting as precisely as possible, and it should be checked at intervals because temperature changes cause a slight drift. Slit and wavelength settings must be identical for all readings.

Make a preliminary reading of the rubidium content of the sample solution, using a calibration

curve prepared from standards all of which contain 1000 ppm of K_2O and 1000 ppm of MgO. Establish the rubidium concentration to the nearest ppm.

Using a standard solution with slightly less rubidium than the unknown, set the variable resistor, the galvanometer controls, and the T knob and dark current control on the DU spectrophotometer so that the galvanometer and the Beckman indicating ammeter read full scale and zero, respectively, both with the shutter open and with it closed. Adjust the sensitivity of the galvanometer circuit so that the index moves full scale with a known increase in the rubidium content of the solution (conveniently 2 or 10 ppm of Rb_2O). The excess Rb_2O in the unknown over that in the standard may then be obtained from the galvanometer scale reading. For small amounts of rubidium (<2 ppm), the relation between galvanometer reading and ppm of Rb_2O is almost linear (Fig. 4); with larger amounts, a calibration curve should be prepared for each 2-ppm range.

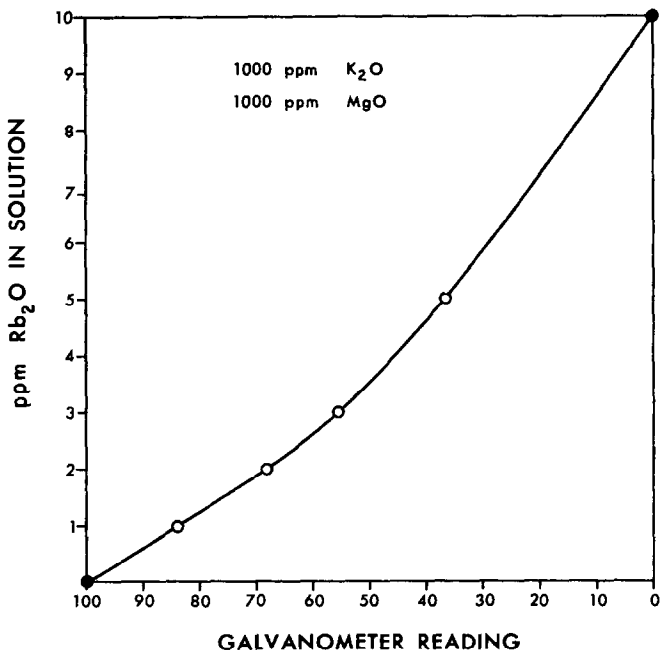


FIG. 4—Working curve for rubidium, 0–10 ppm. The relation between Rb_2O concentration and galvanometer reading is nearly linear up to 2 ppm of Rb_2O. Similar curves may be prepared for Cs_2O and Li_2O. Instrument settings may be adjusted so that the full scale galvanometer reading represents any desired range of the element being determined.

During these measurements, it is best to leave out of consideration the rubidium content of the standard potassium solution, correcting for it later.

Readings made in this way are reproducible, when all adjustments are properly made, to 1 division on the galvanometer scale, corresponding to 0·02 ppm of Rb_2O in solution or 2 ppm in a 0·5-g sample diluted to 50 ml; however, there are six readings or settings involved in a differential determination; two each in establishing (a) the rubidium content of the standard potassium solution, (b) the sensitivity setting against the standard rubidium solution, and (c) the excess rubidium in the unknown over the standard. The actual probable reading error in a differential rubidium determination is therefore close to the equivalent of ±3 divisions, or ±0·06 ppm of Rb_2O in solution. Near the limit of detection, this is reduced to about ±0·04 ppm, because only four readings are involved. This corresponds to ±2 ppm of Rb_2O in a 0·5-g sample diluted to 25 ml.

It is very desirable to check the potassium content of the unknown solution in which rubidium and caesium are determined. This should of course be 1000 ppm. The check is best made by adjusting the DU spectrophotometer controls so that a solution with 1000 ppm of K_2O, 1000 ppm of MgO, and a rubidium content near that of the unknown reads 100 × ·1 on the T scale, and reading the unknown at that setting. The difference should be less than 1 × ·1 T, except with samples which contain much magnesium, which tend to give low readings. If the potassium content of the sample solution appears low, a correction should be made, based on a calibration curve (Fig. 5) giving the variation in apparent

rubidium content with potassium content at the Rb_2O level of the unknown. Such a correction is seldom required if the potassium determination was carefully done, unless an unusually high Rb:K ratio exists in the sample, or much magnesium is present.

The correction for the rubidium content of the standard potassium solution will normally be positive, corresponding to the difference in Rb_2O content between the volume added to the unknown and that containing 50 mg of K_2O. Thus, if the standard potassium solution contains 10,000 ppm of K_2O, and x ml is added to the unknown, the correction is $+(5 - x)R$, where R is the Rb_2O content of the potassium solution. A method of determining this is given above.

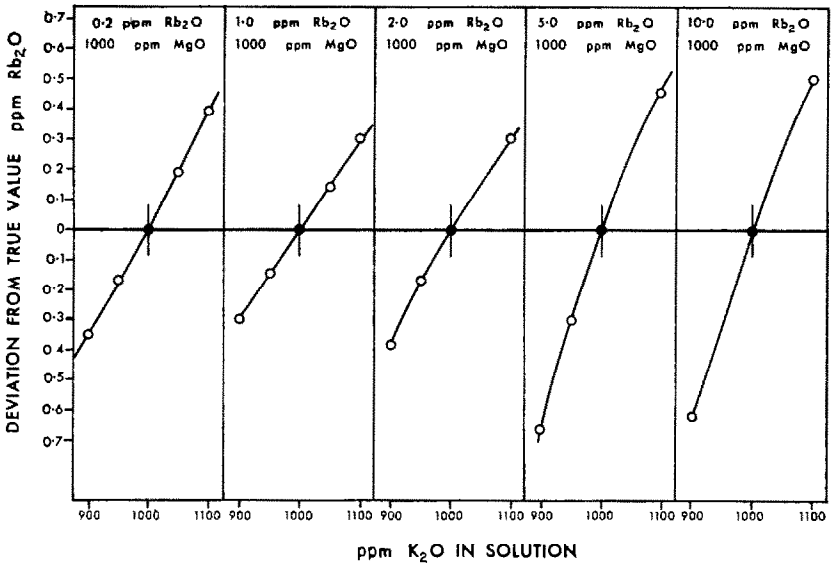


FIG. 5—Effect of potassium concentration on the determination of traces of rubidium. The variation of apparent Rb_2O content with potassium concentration results from a combination of interference and enhancement effects.

Determination of caesium: Caesium may be determined in the same way as rubidium, using a 0·4-mm slit and a wavelength setting near 852 mμ. Maximum sensitivity is about twice that for rubidium, and adjustments can conveniently be made so that a full scale galvanometer reading corresponds to 1·0 ppm of Cs_2O in solution, or 0·01% in the sample. Since in naturally occurring materials, the caesium content is frequently about one-tenth that of rubidium, some of the standard solutions used for the latter may to advantage have caesium added as well, in about a 1:10 ratio. The same set of standard solutions may then be used for both elements.

Little difficulty was experienced with caesium impurity in the potassium salts used, except when attempts were made to determine the element in samples containing 1 ppm or less. It is advisable to determine the caesium content of the standard potassium solution in a manner similar to that described for rubidium.

When the rubidium and caesium determinations are completed, a final reading for potassium should be made on the solution of the 50-mg sample, using standards containing the correct amounts of these elements as well as sodium and magnesium.

Determination of lithium: Add to the solution prepared for the lithium determination enough standard sodium solution to bring its concentration up to a standard value (conveniently 500 or 1000 ppm of Na_2O), and proceed as for rubidium or caesium, using a 0·4-mm slit and a wavelength setting near 671 mμ. If an indicator (methyl red) was added during the preparation of the solution, its sodium content should be taken into consideration; however, the effect of sodium on the lithium determination, while appreciable, does not require as accurate adjustment of the major alkali concentration as is necessary with rubidium and cesium.

RESULTS AND DISCUSSION

Some comparative results are given in Tables I, II and III. In the case of caesium, no comparable method was available, and the procedure was checked by carrying

TABLE I.—COMPARATIVE RESULTS FOR SODIUM AND POTASSIUM

Sample	Na_2O present[a]	Na_2O found	K_2O present[a]	K_2O found
Granitic rock	4·30	4·35	1·01	1·02
Granitic rock	4·69	4·70	1·31	1·32
Granitic rock	4·71	4·70	0·90	0·88
Lepidolite	0·30	0·32	9·88	9·90
Mica	—	—	9·32	9·40
Obsidian	4·28	4·25	4·60	4·60

[a] Separated by Lawrence Smith procedure: potassium weighed as chloroplatinate, sodium by difference from weight of chlorides. Corrections for the minor alkalies determined by flame photometry after conversion of chloroplatinates of potassium and of sodium to sulphates.

TABLE II.—DETERMINATION OF RUBIDIUM IN BIOTITE: COMPARISON OF RESULTS BY FLAME PHOTOMETRY AND BY MASS SPECTROMETRY

K_2O, %	Rb, *ppm*	
	Proposed method	Isotope dilution[a]
8·64	415	430
	406	
	415	
8·18	272	250
		253
8·68	572	549
7·78	694	677
8·96	540	538
	534	531
9·23	587	594
8·84	536	516
	520	
8·35	487	484
8·60	659	688
8·43	359	361
	359	356
		352
9·96	320	289
	319	
	293	

[a] Determined at U.S. Geological Survey laboratories, Washington, D.C., U.S.A.

known amounts of the element through the procedure, using a sample of mica which was salted with measured amounts of caesium sulphate. Rubidium was also added to these samples, and results are given in Table IV. Some results with reference samples are given in Table V.

The methods described have been applied to a variety of silicates and related

TABLE III.—DETERMINATION OF POTASSIUM IN BIOTITE

Sample	K_2O present[a]	K_2O found
KA 272 B	9·08	8·88
KA 76 B	7·02	6·98
KA 14 B	8·20	8·10
KA 48 B	3·50	3·46
KA 320 BM	8·72	8·84

[a] Values reported by Goldich and others.[4]

TABLE IV.—DETERMINATION OF RUBIDIUM AND CAESIUM ADDED TO A SAMPLE OF MICA

Sample	Rb_2O added, %	Rb_2O found, %	Cs_2O added, %	Cs_2O found, %
Mica	none	0·0305	none	0·0000
Mica + Rb, Cs	0·0200	0·0503	0·0040	0·0036
Mica + Rb, Cs	0·0400	0·0703	0·0100	0·0096
Mica + Rb, Cs	0·100	0·136	0·0200	0·0194
Mica + Cs	none	0·0307	0·0300	0·0308
Mica + Rb	0·100	0·132	none	0·0002

TABLE V.—POTASSIUM AND RUBIDIUM DETERMINATIONS IN REFERENCE SAMPLES

Sample	K_2O present, %	K_2O found, %	Rb present, *ppm*	Rb found, *ppm*
Granite G-1	5·52[a]	5·52	220[b]	216
Diabase W-1	0·62[a]	0·62	22[b]	20
Biotite B-3203	9·03[c]	9·00	466[d]	460

[a] Values reported by Goldich and Oslund.[5]

[b] Values recommended by Stevens *et al.*[9]

[c] Determined by Lawrence Smith procedure with flame corrections. A compilation of values obtained on this sample by different laboratories is given by Abbey and Maxwell.[1] The sample was prepared as a reference biotite[8] for laboratories engaged in K-Ar determination.

[d] Isotope dilution value, U.S. Geological Survey.

materials, including micas, feldspars, amphiboles, granites, basalts, shales, clays, frits and glasses. No serious difficulties were encountered with any of these materials. With sedimentary rocks, a preliminary ignition at low temperature to remove organic matter is advisable. Samples containing sulphides are best roasted before acid treatment. Some manganese minerals require the addition of hydrogen peroxide or sulphurous acid at intervals during the solution procedure.

The ignition of alkali sulphates must be carried out under oxidising conditions, or there is a possibility of reducing sulphate to sulphide, particularly if a large amount of material is present in the dish. This may lead to losses of potassium (and presumably of caesium and rubidium) by volatilisation; it also results in solutions of high pH. It is for this reason that the standard alkali salts are assayed as directed and weighed out on the basis of the assay, rather than after direct ignition.

A good test for an oxidising flame may be made by heating a nickel crucible at the correct position in the flame and observing its behaviour. The supply of air to the burner should be increased to the point where the bright metallic nickel surface becomes coated with oxide.

In preparing the sample solutions, it is quite necessary to use a flat-bottom platinum dish and a platinum triangle, particularly with 500-mg samples. If round dishes and silica triangles are used, it may prove difficult, if not impossible, to satisfactorily decompose the metallic sulphates. Re-evaporation of the residue with water, followed by re-ignition, as recommended by Abbey and Maxwell[1] may, however, overcome the difficulty.

It is most advisable to check the standard alkali solutions by pipetting 10 or 20 ml into a platinum dish, adding sulphuric acid, evaporating, igniting, and weighing. This will not only make certain of the alkali concentration, but will give a check on the ignition procedure; the rate of loss of the various alkalies under the actual conditions of heating may be followed, and if it is found to be serious, appropriate steps can be taken. The weighed residual salt should be dissolved in water, and a pH measurement made.

Procedures similar to those described can also be applied to solutions obtained by other chemical techniques, for example the Lawrence Smith method for the separation and collection of the alkali metals.[5] The differential measurement procedure can also be used for the alkaline earth elements, and this technique has been found most useful for the determination of strontium in the presence of large amounts of calcium. Nitrate solutions are used for the alkaline earth elements.

Lithium is not recovered completely by the sulphate ignition procedure described for the other alkalies, nor by the Lawrence Smith procedure, except in the case of certain samples containing no alumina. It is necessary to use a lead carbonate separation for this element, or to follow Horstman's procedure. The lead carbonate procedure is unsuitable for the other alkalies.

Galvanometer stability is improved by grounding the case of the DU spectrophotometer to a water pipe, but the Coleman instrument and its power supply should not be grounded. Instrument drift was found to be caused in part at least by temperature changes, and was largely eliminated by insulating the DU spectrophotometer from the hot flame chimney by means of sheet aluminium, and allowing a 2–3 hr warm-up period before making any settings. The wavelength setting for rubidium is particularly sensitive in this respect, and should be checked before all final readings.

During the differential measurements, and during the caesium determination in particular, the entrance end of the DU spectrophotometer should be shielded from even diffuse daylight, especially when clouds or moving vehicles cause fluctuations in room lighting.

The 1·5-V dry battery in the Coleman Universal spectrophotometer deteriorates rapidly at the sensitivity settings required. The 'Galv-o-meter', which is provided with a mercury battery, might be better in this respect, but the lower voltage will lead to lower sensitivity. The use of two 1·5-V dry batteries in series as recommended is satisfactory.

The differential method of measurement has not been used for rubidium in materials containing more than about 5000 ppm of Rb_2O. Above this amount, flame photometric readings are made by the technique of Horstman,[6] without the use of the galvanometer. With large amounts of rubidium, the preliminary potassium determination is affected to the extent that the 'salting up' to 1000 ppm of K_2O becomes progressively less accurate, to the point where it is difficult to take meaningful advantage of the increased precision of differential measurement.

With samples containing much manganese, appropriate additions of this element should be made to the final standards. The large magnesium addition which is always made during the solution procedure minimises the effect of small amounts of manganese and other foreign elements. Its depressing effect on both rubidium and potassium emission does not seriously affect sensitivity.

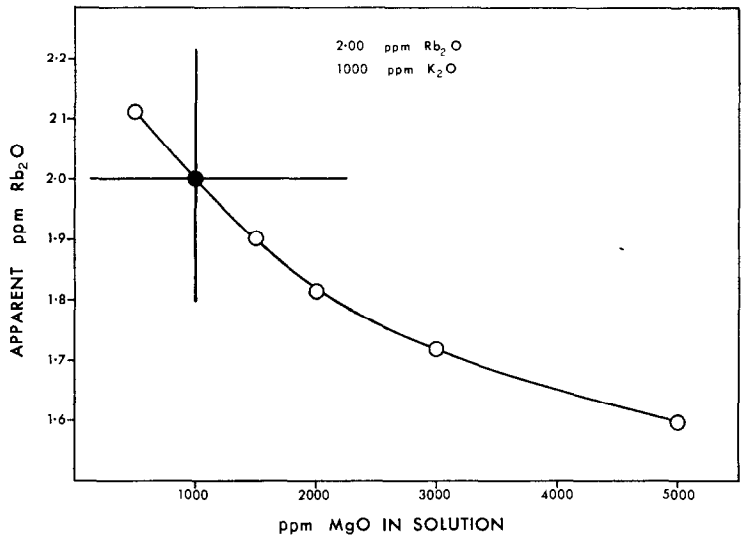


FIG. 6—Effect of magnesium on rubidium emission. Instrument settings are made so that the external galvanometer reads at mid-scale with solutions containing 1000 ppm of K_2O, 1000 ppm of MgO, and the indicated Rb_2O concentration. Variations in apparent Rb_2O content with changes in magnesium concentration are shown.

Large amounts of calcium interfere with the determination of lithium, and highly accurate lithium values can only be obtained if this is taken into account. The amount of calcium in the final solution for lithium determination is, of course, limited by the solubility of calcium in the lead carbonate-sulphate suspension.

The interference of magnesium cannot be entirely overcome unless the magnesium content of the sample is known. However, in most cases the error is small. The effect of magnesium originating in the sample is, of course, greater with the larger samples, and is revealed on checking the potassium content of the 500-mg sample used in the determination of rubidium and caesium. A discrepancy observed at this stage in the procedure may be treated as though it were caused by a deficiency of potassium, even though it is in fact a result of magnesium excess, with satisfactory results so far as the correcting of the rubidium value is concerned. The effect of magnesium on the rubidium emission is shown in Fig. 6.

While results by the techniques described in many cases approach in accuracy and precision those obtained by the most refined methods involving gravimetric determination of the major alkalies and flame photometric determination of the minors, it seems doubtful that any purely flame photometric method can compete with flame-supported gravimetric procedures in the determination of alkali contents in excess of about 5%, except in special cases. It should be noted, however, that procedures following acid attack of the sample have one major advantage over the Lawrence Smith method when applied to hydrous minerals such as biotites. The

sample can be weighed in the unground condition, or after a minimum of grinding, whereas, with many such materials, fine grinding must precede weighing for the Lawrence Smith method. Problems of loss or gain of water and of oxidation of iron^{II} during sample preparation are thus avoided.

Acknowledgment—The author is indebted to S. S. Goldich, Chief, Isotope Geology Branch, U.S. Geological Survey, for invaluable assistance and advice, and for supplying analysed samples which are reported in Tables II and III. Full credit for the basic design of the flame attachment must be accorded R. B. Ellestad, P. T. Gilbert, E. L. Horstman, H. Baadsgaard and other workers in the Rock Analysis Laboratory of the University of Minnesota, where a similar apparatus was used and analytical methods for the alkali metals were developed over a period of many years.

Zusammenfassung—Wenn ein äusserer Gelvanometerstromkreis an ein Beckman DU-Spektrophotometer angeschlossen wird, ist es möglich differentielle Flammphotometrie der Alkalien und alkalischen Erden auszuführen. Eine verbesserte, hochstabile Luft- Naturgas-Flamme muss verwendet werden. Wenn es auch zweifelhaft ist, dass rein flammphotometrische Methoden jemals gravimetrische Genauigkeit erreichen kennen (für Alkalihauptbestandeteile) so wurde immerhin eine Methode ausgearbeitet, durch die Rubidium und Cäsium mit erhöhter Reproduzierbarkeit bestimmt wurden und die Genauigkeit der Natrium- und Kalium bestimmung beträchtlich erhöht wurde.

Résumé—En reliant un circuit galvanométrique externe à un spectrophotomètre Beckman DU et en utilisant une flamme air-gaz naturel très stable, il est possible d'appliquer le principe de la mesure differentielle au dosage par spectrophotométrie de flamme des alcalins et des alcalino-terreux importants et secondaires. Il est douteux que toute méthode par photométrie de flamme raisonnablement rapide puisse jamais égaler les meilleures techniques gravimétriques, dans les dosages des principaux constituants alcalins; cependant des méthodes permettant de doser le rubidium et le césium avec une précision améliorée ont été mises au point, ainsi que d'autres augmentant de façon significative la précision des dosages du sodium et du potassium.

REFERENCES

[1] S. Abbey and J. A. Maxwell, *Chemistry in Canada*, 1960, **12**, 37–41; Reprint 17, Department of Mines and Technical Surveys, Geological Survey of Canada.
[2] R. B. Barnes, D. Richardson, J. W. Berry and R. L. Hood, *Ind. Eng. Chem., Analyt.*, 1945, **17**, 605.
[3] R. B. Ellestad and E. L. Horstman, *Analyt. Chem.*, 1955, **27**, 1229.
[4] S. S. Goldich, A. O. Nier, H. Baadsgaard, J. W. Hoffman and H. W. Kreuger, *Minnesota Geological Survey Bull.* 41, *The Precambrian Geology and Geochronology of Minnesota.* The University of Minnesota Press, Minneapolis, Minn., 1961.
[5] S. S. Goldich and E. H. Oslund, *Geol. Soc. America Bull.*, 1956, **67**, 811.
[6] E. L. Horstman, *Analyt. Chem.*, 1956, **28**, 1417.
[7] *Idem, Geochim. Cosmochim. Acta*, 1957, **12**, 1.
[8] W. H. Pinson, *Annals of the New York Acad. Sci.*, 1961, **91**, Art. 2, 221
[9] R. E. Stevens *et al.*, *U.S. Geol. Survey Bull.*, 1960, 1113.

Talanta, 1962, Vol. 9, pp. 795 to 797. Pergamon Press Ltd. Printed in Northern Ireland

SUBMICRO DETERMINATION OF IRON IN ORGANIC MATERIALS

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Summary—A method for the determination of iron in solid organic compounds, such as ferrocene and its derivatives, has been developed. Sample weights between 25 and 400 μg were used, the optimum sample size being such as to contain between 10 and 20 μg of iron. All results obtained from the analysis of standard compounds were within $\pm 0{\cdot}5\%$ absolute. An indication is given of the utility of working on the small scale in detecting inhomogeneity of materials.

RECENT reviews of small-scale organic analysis have been given by Belcher,[1] using 30–50 μg samples, and by Kirsten[2] who used sample weights of about 500 μg. Several potential methods for the determination of iron in the range 10 to 100 μg existed. It appeared reasonable, therefore, to attempt the determination of iron in ferrocene derivatives, where iron contents between 5 and 30% were expected, using sample weights within the range covered by these two workers.

Titrimetric and colorimetric techniques only were considered for the determination of iron. Of the former, potentiometric titration with 0·01*N* mercury[I] nitrate,[3] under a nitrogen atmosphere, showed promise (deviations on one day of $\pm 0{\cdot}2$ μg of iron) but it was found that the titrant needed frequent restandardisation. Photometric titration with the apparatus available was not sufficiently sensitive although results to $\pm 0{\cdot}4$ μg of iron were achieved by titration with 0·05*M* EDTA at pH 3·5 using potassium thiocyanate or sulphosalicylic acid as indicator.

Of the many colorimetric reagents available, previous experience indicated that 1:10-phenanthroline would be most likely to meet the requirements. Indeed, it was found, both during preparation of the calibration curve and also during checks using independently prepared standard iron solutions, that a precision of $\pm 0{\cdot}1$ μg could be expected in the range 5 to 25 μg of iron using 4-cm fused silica absorption cells in a spectrophotometer.

EXPERIMENTAL

Procedure

Weigh by difference,[4] on the submicro balance[5] sufficient of the sample to give between 5 and 25 μg (optimum 10 to 20 μg) of iron and transfer from the platinum weighing boat into a hard glass digestion tube (9 mm internal diameter, 12.5 mm external diameter, 8 cm long). Add 0.1 ml of acid digestion mixture (95 ml of conc. nitric acid + 5 ml of conc. sulphuric acid) and seal off the tube with a blowpipe flame. Place the sealed tube vertically in a metal rack and transfer to an oven at 300 ± 20°. After 1 hr, remove the rack and allow to cool. Release pressure in the tube by heating the tip in a blowpipe flame. Place the digestion tube in a larger glass tube on a steam bath and apply suction (water pump) to remove volatile material. Remove the digestion tube, allow to cool and cut off the top in the usual way. Wash the contents of the tube and its top into a 25-ml volumetric flask (via a 25-ml beaker) with distilled water. Add 2 ml of hydroquinone (1% aq.), 2.5 ml of acetate buffer (225 ml of 2*N* acetic acid + 25 ml of 2*N* sodium acetate) and 2 ml of 1:10-phenantholine (0.25% aq.), swirling between additions. Make up to the mark with distilled water, mix and leave for 1 to 1.5 hr. Measure the optical density, at 509 mμ, in 4-cm cells* against a reagent blank. Compute the iron in the flask from a calibration curve prepared after similar development of standard iron solutions.

* When a sample is found to contain over 25 μg of iron the use of matched 2-cm or 1-cm cells is recommended.

RESULTS

Table I shows the results obtained after the analysis of four compounds using the procedure described and illustrates the range of weights that may be taken. A high proportion of the results lie within ±0·2% absolute and none are more than ±0·5% in error. It would appear that the dicarboxylic acid may not have been quite pure.

TABLE I—ANALYSIS OF COMPOUNDS

Compound	Range of sample wt., μg	Iron, %		No. of detns.	Standard deviation	Range of errors, %
		Calc.	Found (mean)			
Ferrocene	29·4–157·8	30·02	30·11	8	0·27	−0·34 to +0·43
1,1′-Dibenzoyl ferrocene	44·0–158·0	14·17	14·22	8	0·12	−0·15 to +0·23
Ferrocene 1,1′-dicarboxylic acid	63·4–99·3	20·38	20·13	8	0·14	−0·45 to −0·10
Ferrocene 1,1′-dicarboxyanilide	50·5–179·6	13·16	13·21	10	0·21	−0·30 to +0·40

Because of the volatility of ferrocene, which caused weighing difficulties with finely divided samples, the results quoted above were obtained from the analysis of material sublimed to give small but dense crystals. As a further precaution against loss, the crystals were dropped straight into digestion acid previously pipetted into the glass tubes.

The results from analysis of research materials are given in Tables II and III.

TABLE II—ANALYSIS OF RESEARCH MATERIALS

Material	Range of sample wt., μg	Iron found (mean), %	No. of detns.	Deviations from mean, %
A	55·1–156·8	19·60	4	−0·18 to +0·17
B	38·0–299·3	13·63	8	−0·18 to +0·25
C	38·3–151·8	18·91	5	−0·18 to +0·28
D	162·7–220·6	6·60	3	−0·05 to +0·10

The results on materials A to D (Table II) were selected to illustrate the reproducibility attainable over a wide range of sample weights and on relatively high and low iron contents. It will be seen that all of the results lie within ±0·3% of the mean, even over the 40 to 300-μg sample range taken for compound B. This not only indicates the precision of the method, but also that the materials as submitted for analysis were homogeneous.

Considering now materials E to G (Table III), some erratic results are found. E was an unpurified sample of diacetyl ferrocene and it can be seen that four results are within ±0·3% of the theoretical (20·68% of iron). The other two are, however, over 1% high. F gave the even more striking result of 25·49% for one sample whereas the other five results lie within ±0·3% of the mean, 1·17%. Material G gave two results which are in reasonable agreement but the other two are more scattered than would be expected.

TABLE III—ANALYSIS OF OTHER RESEARCH MATERIALS

E	Wt. taken, μg	45·9	48·3	58·0	77·9	96·1	111·4
	Fe found, %	20·56	20·97	21·70	20·72	20·78	23·32
F	Wt. taken, μg	113·7	137·1	160·2	166·6	345·1	386·7
	Fe found, %	1·12	1·46	1·12	1·14	25·49	1·03
G	Wt. taken, μg	66·4	109·0	141·9	154·1		
	Fe found, %	23·87	23·66	21·95	26·19		

It is considered that these scattered results are not caused by any failure of the method but are rather an indication of inhomogeneity in the materials. An example was provided by the analysis of some commercially produced ferrocene where three crystals, varying in weight between 40 and 97 μg, gave iron contents of 29·6 $\pm$ 0·1% but a fourth, which was selected because of its slightly different colour and texture, gave 26·6% of iron.

Providing that sufficient precision is attainable on homogeneous samples, we suggest that the ability to work on the submicro scale has an added advantage in that the presence of impurities or mixtures may be detected by replicate analyses of the sample, or, more specifically, by analysis of suspect particles separated from the main bulk of the sample. This may be particularly useful in research on intractable polymeric materials.

Acknowledgements—We are indebted to Professor R. Belcher for an introduction to the techniques of submicro analysis and to Mr. E. J. P. Fear and Dr. W. A. Lee for the provision of samples.

Zusammenfassung—Eine Methode zur Bestimmung von Eisen in festen organischen Verbindungen, wie z.B. Ferrocen und seinen Derivaten wurde ausgearbeitet. Probenmengen von 25–400 μg wurden verwendet, wobei das Optimum bei einer Menge liegt, die etwa 10–20 μg Fe entspricht. Alle Ergebnisse mit Standardkomponenten waren inner halb einer Fehlergrenze von $\pm$0·5% absolut. Es wird auf die Möglichkeit verwiesen unter Verwendung von so kleinen Probenmengen Inhomogenitäten in Präparaten nachzuweisen.

Résumé—Les auteurs décrivent une méthode de dosage du fer dans les composés organiques solides du type ferrocène et de ses dérivés. Des poids d'échantillon compris entre 25 et 400 μg ont été utilisés, le poids optimal de l'échantillon étant tel qu'il contienne de 10 à 20 μg de fer. La précision de la méthode est de l'ordre de $\pm$0,5 pour 100. Le fait d'opérer sur des prises d'essai très petites permet de mettre en évidence l'hétérogénéité des produits utilisés.

REFERENCES

[1] R. Belcher, *Proceedings of* 1961 *International Symposium on Microchemical Techniques.* Interscience, New York, in press.
[2] W. J. Kirsten, *ibid.*
[3] R. Belcher and C. L. Wilson, *New Methods in Analytical Chemistry.* Chapman and Hall, London, 1955, p. 183.
[4] T. R. F. W. Fennell and J. R. Webb, *Proceedings of* 1961 *International Symposium on Microchemical Techniques.* Interscience, New York, in press.
[5] F. Jasim, R. J. Magee and C. L. Wilson, *Mikrochim. Acta*, 1960, 721.

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SHORT COMMUNICATIONS

New colour reactions of elemental sulphur and carbon disulphide*

(*Received* 19 *December* 1960. *Accepted* 18 *February* 1961)

IT is often desirable to detect minute quantities of elementary sulphur in inorganic or organic raw materials, intermediates or finished products, and some attention has recently been devoted to this problem.[1,2] An excellent colorimetric determination has also been described.[3,4]

The present author has found that a solution of sulphur in acetone gives a transient green (at higher concentrations) or blue (at lower concentrations) colour when shaken with concentrated aqueous sodium or potassium hydroxide.

If the acetone is replaced by methyl ethyl ketone or methyl *n*-propyl ketone, a yellow colour develops on adding concentrated aqueous sodium or potassium hydroxide. The colour is stable and can serve for the colorimetric determination of sulphur, but the reaction is less sensitive than that with acetone.

When acetone and potassium hydroxide, but *not* sodium hydroxide, are used and the green or blue colour has disappeared, the addition of 1 drop of carbon disulphide produces a pink colour. This is more stable than the original green or blue and can be used to detect carbon disulphide.

Both reactions can be used to detect elementary sulphur in inorganic (*e.g.* gypsum) or organic (*e.g.* hydrocarbons) compounds.

Interferences

Sulphur-containing compounds, such as sodium sulphide, hydrogen sulphide, sodium hydrosulphide, sodium thiosulphate, thiophene, 2-aminothiazol, thiourea, do not give the green or blue colour. The presence of selenium does not interfere with the reaction. A large quantity of water in the acetone reduces the sensitivity of the test. No change of sensitivity was, however, observed when the content of water in acetone was below 10%. Therefore it is not necessary to use anhydrous acetone. A large quantity of ethyl alcohol (above 25%) also reduces the sensitivity of the test.

Neither water nor ethyl alcohol interferes with the pink colour developed on adding carbon disulphide. The presence of some organic compounds (*e.g.* thiourea) in the acetone solution interferes with the reaction. In such cases only a yellow colour appears.

EXPERIMENTAL

Reagents

0·01% *w/v Standard sulphur solutions:* Prepared by dissolving 20 mg of pure sulphur (pharmaceutical grade, recrystallised twice from carbon tetrachloride, m.p. 118°) in 200 ml of pure acetone, petroleum ether (boiling range: 75–110°; density: 0·73 at 25°), iso-octane, *n*-heptane and cyclohexane, respectively.

0·1% *Standard carbon disulphide solution:* Prepared by dissolving 1 g of pure carbon disulphide in 1 litre of pure acetone.

30% *Sodium and potassium hydroxide solutions:* Prepared by dissolving 300 g of sodium and potassium hydroxide, respectively, in distilled water followed by dilution to 1 litre.

Detection of sulphur in acetone solution

To a few ml of a solution of sulphur in acetone add a few ml of 30% aqueous potassium hydroxide and shake. When the concentration of sulphur in the solution is 0·01%, a dark grass-green colour develops in the acetone layer. A still higher concentration produces an olive-green colour. When the concentration is lower (0·001%), the colour is blue. The limit of sensitivity of the reaction is about 0·0002% of sulphur. No colour was observed when the concentration of sulphur was 0·0001%.

* This work was completed in 1957, but for various reasons publication was delayed. In the meantime a similar test for the detection of elementary sulphur by means of acetone was described by G. Ingram and B. A. Toms, *Analyst*, 1960, **85**, 766.

After the green or blue colour fades, add 1 drop of carbon disulphide and shake. If the concentration of sulphur in acetone is relatively high (0·01 %), a strawberry colour appears. When the concentration is low (0·001 %), a light pink colour appears. At a higher concentration (0·05 %) an orange colour is formed. It is less characteristic than the colour developed at lower concentrations.

The colour appears within 0·5–2 min after adding the carbon disulphide and its intensity increases with time. The highest intensity is acquired after 3–5 min, and the colour fades within 20–30 min.

Detection of sulphur in hydrocarbons with acetone

Dilute 1 litre of the solution of sulphur in hydrocarbon (*e.g.* petroleum ether, iso-octane, *n*-heptane, cyclohexane) with pure acetone to 7–8 ml, then add 1–2 ml of 30 % aqueous potassium hydroxide. A green (at higher concentrations of sulphur in the solution) or blue (at lower concentrations) colour develops. Sulphur in a concentration as low as 0·002 % in the hydrocarbon can be detected.

After the colour fades, add 1 drop of carbon disulphide. A pink colour varying in intensity from light pink at lower concentrations to strawberry at higher concentrations (0·05 % of sulphur in hydrocarbon) develops within a few min, reaching its maximum intensity after 3–5 min and lasting for about 30 min.

Detection of sulphur in hydrocarbons with methyl ethyl ketone or methyl n-propyl ketone

Dilute 1 ml of the solution of sulphur in hydrocarbon with 5 ml of methyl ethyl ketone or methyl *n*-propyl ketone and add 1–2 ml of 30 % aqueous sodium or potassium hydroxide. A yellow colour develops in the ketone solution. The sensitivity limit is of the order of 0·05 % of sulphur in hydrocarbon.

Detection of carbon disulphide

Add the solution of 0·01 % of sulphur in acetone to the same volume of solution of carbon disulphide in acetone, then add 30 % aqueous potassium hydroxide. A greenish-blue colour caused by the presence of sulphur in acetone develops and quickly disappears, then a strawberry or pink colour appears in the acetone layer within 5–10 min. This colour lasts for 20 min to 1 hr and finally changes to yellow. The sensitivity limit of the reaction is of the order of 0·01 % of carbon disulphide in acetone.

The potassium hydroxide layer is at the same time coloured yellow as a result of the formation of potassium trithiocarbonate.

The method can be applied to the detection of carbon disulphide in air. The air is drawn through a train of three or four tubes, containing a solution of 0·01 % of sulphur in acetone cooled to 0–5°, at a rate of about 0·1 litre per min. The solution in the first two tubes is subsequently combined and tested with 30 % aqueous potassium hydroxide as above.

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Summary—Simple colour reactions are described for the detection of elementary sulphur and carbon disulphide.

Zusammenfassung—Einfache Farbreaktionen werden beschrieben, mittels derer elementarer Schwefel oder Schwefelkohlenstoff in azetonischer Lösung nachgewiesen werden können.

Résumé—L'auteur décrit des réactions colorées simples par lesquelles le soufre élémentarie ou le sulfure de carbone en solution dans l'acétone peut être décelé.

REFERENCES

[1] Fritz Feigl, *Spot Tests in Organic Analysis*. Elsevier Publishing Co., Amsterdam, 3rd ed., 1956.
[2] H. Levin, *Analyt. Chem.*, 1953, **25**, 47.
[3] J. K. Bartlett and D. A. Skoog, *Analyt. Chem.*, 1954, **26**, 1008 and 1955, **27**, 369.
[4] A. Castiglioni, *Gazz. chim. ital.*, 1933, **63**, 171.

The determination of gallium

(*Received* 29 *November* 1961. *Accepted* 12 *January* 1962)

DETERMINATION OF GALLIUM IN PURE SOLUTIONS

CLASSICAL methods for the determination of gallium were invariably completed by a gravimetric procedure involving precipitation of either hydroxide or cupferrate, followed by ignition to the oxide

After the green or blue colour fades, add 1 drop of carbon disulphide and shake. If the concentration of sulphur in acetone is relatively high (0·01 %), a strawberry colour appears. When the concentration is low (0·001 %), a light pink colour appears. At a higher concentration (0·05 %) an orange colour is formed. It is less characteristic than the colour developed at lower concentrations.

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REFERENCES

[1] Fritz Feigl, *Spot Tests in Organic Analysis*. Elsevier Publishing Co., Amsterdam, 3rd ed., 1956.
[2] H. Levin, *Analyt. Chem.*, 1953, **25**, 47.
[3] J. K. Bartlett and D. A. Skoog, *Analyt. Chem.*, 1954, **26**, 1008 and 1955, **27**, 369.
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The determination of gallium

(*Received* 29 *November* 1961. *Accepted* 12 *January* 1962)

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CLASSICAL methods for the determination of gallium were invariably completed by a gravimetric procedure involving precipitation of either hydroxide or cupferrate, followed by ignition to the oxide

Ga_2O_3.[1] Several titrimetric procedures using an excess of EDTA and a variety of titrants and indicators have been described[2] and direct titrations with EDTA have also been reported.[3–5]

When the direct determination of gallium using 0·01*M* EDTA was attempted, difficulty, in the form of delayed end-points, was experienced. This was particularly noted in cold solution. The replacement of EDTA by CyDTA gave no significant improvement.

Using morin as indicator, it was observed that an increase of fluorescence under ultraviolet light could be obtained by decreasing the pH of the solution from 4·0 to 1·7, for example by omitting the borax and sodium fluoride from the buffer solution described by Doležal *et al.*[4] A similar result was obtained by neutralizing the gallium solution to methyl red, and adding acetic acid to bring the solution to pH2. It was also noticed that the trace of red indicator colour effectively masked the slight residual fluorescence, and hence sharpened the end-point.

An increase in the fluorescence produced by gallium with morin was noted when certain water-miscible organic liquids were added to the solution. This is shown in Table 1. In all subsequent work equal volumes of methanol were added to the gallium solutions before titration.

Table I

Additive	Fluorescence	End-point	Gallium recovered,† *mg*
ethanol	good	delayed	6·99
iso-propanol	good	very poor	6·32
dioxan	good	slightly delayed	6·92
acetone	good	*normal	6·92, 6·92, 6·89
methanol	good	*normal	6·92, 6·92, 6·92 6·89, 6·96

* *i.e.* End-point in the absence of organic additive.

† Aliquots of a stock solution containing approximately 6·9 mg of Ga were used in each case.

A small amount of morin obtained in the early nineteen thirties was available for these determinations. This was a pale-buff powder giving a pale-yellow solution in methanol. More recent supplies of morin have been iridescent, black, crystalline materials giving brown solutions in methanol that do not fluoresce appreciably with gallium. Morin obtained from Dr. Theodor Schuchardt, G.m.b.H., Munich, however, compares very favourably with the pre-war material.

None of these improvements has significantly reduced the delay in reaching an end-point, although the increased fluorescence had made the end-point easier to detect. It is also possible to titrate in daylight, using only a small box to surround the vessel and ultraviolet lamp. On bright days it is possible to dispense with the lamp altogether. The quantitative recovery of gallium from a number of standard solutions by this procedure is shown in Table II.

Table II

Gallium taken, *mg*	Gallium recovered, *mg*
0·14	0·15*
0·35	0·38*
0·70	0·72,* 0·70,* 0·72
1·39	1·41,* 1·41
1·74	1·76
3·49	3·49
6·97	6·97, 6·96, 6·96
13·94	13·92, 13·81, 13·81
17·43	17·37

* By titration using 0·001*M* EDTA

SEPARATION FROM INTERFERING ELEMENTS

The presence of even a small amount of fluoride ion was found to quench the fluorescence at the pH2 used. Doležal *et al.* added sodium fluoride to remove the interference from aluminium, which also fluoresces with morin. This interference can, however, be eliminated by effecting a prior separation. A method for doing this had been described by Swift,[6] based upon repeated extraction of gallium from 6*M* hydrochloric acid with ether. An improved procedure for this extraction is described by Milner.[3]

An alternative although slightly longer procedure has now been devised following the work of Kraus *et al.*,[7] using strongly basic anion-exchange resins. These resins, used in the form of columns 1 cm in diameter and 4 cm in length, absorb gallium from 6*M* hydrochloric acid solution together with iron, zinc, cadmium, mercury, thallium, tin, antimony^{V} and bismuth. On washing the columns with 1*M* hydrochloric acid the gallium is removed, together with the iron^{III} and the antimony^{V}. It is therefore possible to separate gallium from all the other elements by this procedure, provided that iron and antimony are reduced to their lower valency states before passage through the ion-exchange column. For this purpose a silver reductor is employed.[1]

This method of separation has been used in the determination of the gallium content of Bayer liquor, containing approximately 40 g of aluminium per litre.

Procedure

Ten ml of the Bayer liquor were diluted to 20 ml with water and neutralized, and the acid strength was then increased to 6*M* with concentrated hydrochloric acid. This solution was passed through a silver reductor (6 cm in length, 1 cm in diameter), which was washed with 20 ml (about 3 column volumes) of 6*M* hydrochloric acid. The combined eluate and washings were immediately rinsed on to an anion-exchange column 4 cm in length (Dowex 1 × 4, 100–200 mesh) and the column was eluted with 60 ml (about 20 column volumes) of 6*M* acid. The gallium was eluted with 20 ml (about 6 column volumes) of 1*M* hydrochloric acid.

The eluate was carefully neutralised to methyl red with 10% aqueous sodium hydroxide, and 10 ml of glacial acetic acid were added. The volume was increased to 50 ml by dilution with water, and 50 ml of methanol were added. The solution was titrated with standard EDTA in ultraviolet light, using morin as indicator, until the vivid fluorescence was extinguished. Aliquots of the Bayer liquor to which additional gallium had been added were also analysed by this procedure. The results obtained are given in Table III.

Table III

Gallium added, *mg*	Gallium recovered, *mg*
nil	0·24,* 0·24*
	0·21,* 0·21*
6·92	7·11, 7·07
13·84	14·00, 14·00

* Titration with 0·001*M* EDTA

Acknowledgements—This note describes part of a research programme of Warren Spring Laboratory D.S.I.R. and is published by permission of the Director.

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Summary—An improved separation of gallium from other elements, using an ion-exchange column, and subsequent determination of the element by titration with EDTA, using morin as indicator, are described. The method has been applied to determination of gallium in the presence of a large excess of aluminium.

Zusammenfassung—Eine verbesserte Trennung fur Gallium vo anderen Elementen wird beschrieben. Ionenaustausch wird eingesetzt und Gallium wird mit ADTE titiert unter Verwendung von Morin al, Indicator. Die Methode wurde zu Bestimmung von Gallium in Gegenwart von grossen Mengen Aluminiums verwendet.

Résumé—Les auteurs décrivent une méthode de séparation du ga'lium d'autres éléments par échange d'ions, suivie d'un titrage par l'E.D.T.A avec le morin comme indicateur. La méthode a été appliquée au dosage du gallium en présence d'un grand exces d'aluminium.

REFERENCES

[1] W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*. J. Wiley and Sons, New York, 2nd Ed., 1953.
[2] F. J. Welcher, *The Analytical Uses of EDTA*. Van Nostrand, New York, 1958.

[3] G. W. C. Milner, *Analyst*, 1955, **80**, 77.
[4] J. Doležal, V. Patrovský, Z. Šulzek and J. Švasta, *Chem. Listy*, 1955, **49**, 1517; *Chem. Abs.*, 1956, **50**, 104.
[5] R. H. A. Crawley, *Analyt. Chim. Acta*, 1958, **19**, 540.
[6] E. H. Swift, *J. Amer. Chem. Soc.*, 1924, **46**, 2375.
[7] K. A. Kraus, F. Nelson and G. W. Smith, *J. Phys. Chem.*, 1954, **58**, 11.

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NOTICES

(Material for this section should be sent directly to the Associate Editor)

CZECHOSLOVAKIA

October 1962: **Seminary on Radiation Detectors:** *Association for Spectral Analysis.* Liblice.

POLAND

Saturday 20 *October* 1962: **Symposium on Chromatography in Analysis and Preparation of Alkaloids:** *Chromatographic Subcommittee of the Analytical Chemistry Commission, Polish Academy of Sciences.* Poznań (see *Talanta*, 1962, **9**, 627).

SWITZERLAND

Monday–Saturday 15–20 *October* 1962: **Second International Exhibition and Congress of Laboratory, Measurement and Automation Techniques in Chemistry.** Swiss Industries Fair, Basle (see *Talanta*, 1962, **9**, 627).

UNITED KINGDOM

Friday–Saturday 21–22 *September* 1962: **Joint Meeting** of *Society for Analytical Chemistry, Microchemistry Group* and *Royal Institute of Chemistry, Dublin and District Section.* Trinity Hall, Dartry Road, Dublin 6.

The following programme has been arranged:

Friday 21 *September*

3.00 p.m. Visit to the Distillery of John Jameson and Sons.

8.00 p.m. Meeting in Trinity Hall on *Modern Trends in Small-Scale Inorganic Analysis*, with the following speakers: Professor T. S. WHEELER, Mr. C. WHALLEY, Mr. R. C. CHIRNSIDE, Dr. R. A. CHALMERS and Dr. D. J. HINGERTY.

Saturday 22 *September*

9.30 p.m. All-day tour by courtesy of Bordna Mona (the Peat Board).

9.00 p.m. Discussion meeting in Trinity Hall on *Modern Trends in Analysis.*

British Standards Institution has announced the following *Revised British Standard:*

B.S. 658: 1962: *Apparatus for the determination of distillation range (including flasks and receivers).* This specifies distillation flask (7 sizes), receiver (5 sizes), thermometer, draught screen (2 types), asbestos adaptor boards, wire gauze, heater (gas or electric), condenser (3 types), retort stand for a wide range of standard distillation tests. The section on flasks represents a revision of the former B.S. 571, and covers material, construction, dimensions and inscriptions. The dimensions ensure that the position of the side tube (and therefore of the thermometer), in relation to the top of the neck and the liquid surface when the flask is ready for use, is the same for all sizes of flask.

The section on receivers represents a revision of the former B.S. 605 and covers material, construction, tolerances, dimensions, graduation of scale and inscriptions, for both the cylindrical type and the Crow type with a conical lower portion. A standard method for determination of capacity is included as an appendix.

The correction of barometric readings to standard temperature and pressure is described in an appendix, which enables distillation temperatures to be corrected in accordance with the specification for the particular liquid concerned. (Price 8s. 6d.).

The following *Amendment Slip* is also announced:

B.S. 3406: *Methods for the determination of particle size of powders: Part* 1: 1961: *Sub-division of gross sample down to* 0.2 *ml. Amendment No.* 1: *PD* 4605.

UNITED STATES OF AMERICA

On 2 July, 1962, Dr. NICHOLAS CHERONIS was fatally injured as a result of an automobile accident. Born in Sparta, Greece, Professor Cheronis arrived in the United States as a boy of fifteen to join his family which had already settled in Chicago. After earning his doctorate at the University of Chicago in 1929, he taught in the Chicago City College system until 1949. He joined the Brooklyn College Faculty the following year as Chairman of the Department of Chemistry.

He was the author of numerous articles and books in his field. Among his books are listed *Organic Chemistry, Semimicro and Macro Organic Chemistry*, and *Semimicro Experimental Organic Chemistry*. He was Chairman of the Editorial Board of *The Microchemical Journal*, which has its office at Brooklyn College. Professor Cheronis was a member of Sigma Xi, the American Chemical Society, the Illinois Academy of Science, the New York Academy of Sciences, the American Association for the Advancement of Science and the Metropolitan Microchemical Society.

He leaves his wife, Mrs. Nicholas Cheronis, and two children, both married, Dion, who lives in Chicago, and Mrs. Peter Selz, who resides in Manhattan.

Sunday 30 *September–Friday* 5 *October* 1962: **ASTM Fourth Pacific Area National Meeting:** *American Society for Testing and Materials.* Statler Hilton Hotel, Los Angeles, California.

The provisional technical programme contains the following items of interest to analytical chemists.:

Monday 1 *October*

9.00 a.m. *Symposium on Cleaning and Materials Processing for Electronics and Space Apparatus—Air Borne Contaminant Session*

A Review of the Gravity Settling Technique for Measuring Dust in Electron Device Processing Areas.	E. E. SELBY
A Comparison of Dust Count Data Obtained from Different Measuring Methods.	R. C. MARSH
Enumeration of Air Borne Particulate Matter by the Scattered Light Technique.	J. F. PUDVIN
Proposed Referee Method for Sizing and Counting of Air Borne Particulate Contamination in Clean Rooms and Other Dust Controlled Areas.	R. A. COTTON

2.00 p.m. Symposium continued—*Solvents and Processing Liquids Session*

Comparative Investigation of Methods of Producing Ultra-Pure Water.	V. C. SMITH
The Silting Index—An Evaluation of Micron and Sub-Micron Contamination in Industrial Waters.	J. L. DWYER
Resistance Measurements as a Means of Controlling the Quality of Ultra-Pure Organic Solvents.	S. BALSBAUGH and V. C. SMITH

Tuesday 2 *October*

9.00 a.m. Symposium continued—*Ultrasonic Analytical Techniques Session*

An Instrument for the Contactless Measurement of Minority-Carrier Lifetime.	C. G. CURRIN and F. A. SMITH
Resistivity Measurements by Thermal Compression Bonding.	L. J. DROEGE
Theory and Performance of a Continuous Electrochemical Detector for Microgram Quantities of Atmospheric Cyanide.	C. O. THOMAS
Measurement of Mass Using Quartz Crystal Resonators.	C. D. STOCKBRIDGE and A. W. WARNER

Wednesday 3 *October*

9.00 a.m. *Symposium on Applied Statistics in Materials Testing*

Proposed Recommended Practice for Interlaboratory Study of a Test Method.	G. WERNIMONT and J. MANDEL
Proposed Recommended Practice on Definitions of the Terms Precision and Accuracy as Applied to Measurement of a Property of a Material.	R. B. MURPHY
Reliability Testing.	E. P. COLEMAN

Thursday 4 *October*

2.00 p.m. *Symposium on Industrial Water*

Methods of Determining Nitrates in Water.	E. GOLDMAN
Application of the Technicon Auto Analyser to Steam Plant Boiler Silica Analysis.	R. C. ALLEN
Recent Advances in Automatic Colorimetric Analysis.	J. F. BAIRD
Water Analysis—As Interpreted by the Equipment Manufacturer.	W. C. BURNS

Friday 5 *October*

9.00 a.m. *Symposium on Advancement in Methods of Air Pollution Measurement*

Particulate Air Contaminants from Combustion.	B. D. TEBBENS
A Light Scattering Instrument for the Determination of Plume Opacity.	L. F. DIXON and H. H. SONDERLING

2.00 p.m. Symposium continued

Methods for the Determination of the Size and Mass Distribution of Aerosols.	A. GOETZ and T. KALLAI
Quantitative Analysis by Gas Chromatography of NO and NO_2 at Low Concentrations in the Presence of Nitrogen.	W. H. CORCORAN
Methods of Analysis, Available and Needed, for Evaluation of a Fluoride Pollution Problem.	R. H. WADE, H. M. BENEDICT and J. M. ROSS

Further information may be obtained from ASTM, 1916 Race Street, Philadelphia 3, Pennsylvania.

Monday–Friday 8–12 *October* 1962: **Twelfth Annual Instrument Symposium and Research Equipment Exhibit:** *National Institutes of Health.* Bethesda, Md.

During the scientific meeting, noted investigators will report on recent trends and developments in research methods and instrumentation. Symposium discussion topics will range from new ion-exchange techniques through nuclear magnetic resonance, optical masers, vacuum ultraviolet, X-ray microscopy, automation in chemical and biochemical research, physiological monitoring, and X-ray diffraction studies of proteins.

For additional information write to JAMES B. DAVIS, National Institutes of Health, Public Health Service, Bethesda 14, Maryland.

Tuesday–Thursday 9–11 *October* 1962: **Sixth Conference on Analytical Chemistry in Nuclear Reactor Technology** and **Third Conference on Nuclear Reactor Chemistry:** *Oak Ridge National Laboratory.* Gatlinburg, Tennessee (see *Talanta*, 1962, **9**, 471).

The preliminary programme for the **Conference on Analytical Chemistry** is as follows:

Tuesday 9 *October*

Morning—*Radiochemistry and Nucleonics Session*

Activation Analysis with a Research Reactor—New Developments.	V. P. GUINN
Identification and Comparison of Physical Evidence for Enforcement Purposes by Neutron Activation Analysis.	L. C. BATE, G. W. LEDDICOTTE and M. J. PRO
The Texas A. and M. Mark I-Ia, Automatic Reactor and Computer-Coupled System for Activation Analysis.	L. E. FITE and R. E. WAINERDI
Determination of Germanium in Mineral Specimens by Neutron Activation Analysis.	M. A. WAHLGREN and K. ORLANDINI
Precise Method for Determination of ^{235}U by Neutron Activation Analysis.	H. BUSSELL, C. L. ZYSKOWSKI and L. C. NELSON, JR.
Analysis of Beryllium in Beryllium Metal by Activation Analysis.	F. W. POSTMA, JR. and C. S. MCMURRAY, JR.
Radionuclides found at Equilibrium Conditions in Cooling Water of 5-Megawatt Pool-Type Research Reactor.	J. R. PELRINE

Afternoon—*Instrumentation Session*

Beta-Excited X-Rays in Analytical Chemistry.	R. H. MÜLLER
Absorptiometry with Beta-Excited X-Rays.	D. C. MÜLLER
Modified X-Ray Diffractometer for Medium-Level Radioactive Samples.	W. A. RYDER, G. V. WHEELER, H. H. LEIGH and F. W. SCHULTZ
Microscope for Ultrahigh Temperatures.	D. M. OLSON

An In-Line Instrument for Automatic Determination of Gases in Simulated Boiling Water Reactor and Steam Loops.	M. SIEGLER and D. T. SNYDER
Comparative Condensation-Pressure Analyser for Vapour Purity of Uranium Hexafluoride.	W. S. PAPPAS, S. A. MACINTYRE and C. W. WEBER
Determination of Hydrogen in Uranium, Utilising a Thermal Conductivity Detector.	D. E. SEIZINGER, L. A. FERGASON and C. H. MCBRIDE

Spectrophotometry Session

Determination of Micro Quantities of Dibutylphosphate in Tributylphosphate-Kerosene.	M. A. WADE and S. S. YAMAMURA
Determination of Tungsten in Reactor Materials—Extraction and Spectrophotometric Determination with 8-Quinolinol.	A. R. EBERLE
Spectrophotometric Determination of Technetium with 1,5-Diphenylcarbohydrazide.	F. J. MILLER and H. E. ZITTEL
Separation and Spectrophotometric Determination of Technetium in "Fission".	R. J. MEYER, R. P. LARSEN and R. D. OLDHAM

Wednesday 10 *October*

Morning—*Spectroscopy Session*

Advances in Atomic Emission Spectrochemistry.	P. T. GILBERT, JR.
The Copper-Spark Method for Spectrographic Analysis—Twenty Years Experience.	J. FARIS
Spectral Excitation of Solutions Using Stable Plasma Jets.	L. E. OWEN
Collection and Flame Photometric Determination of Caesium.	C. FELDMAN and T. C. RAINS

Afternoon—*Analytical Chemistry and the Actinides Session*

Plutonium Sulphate Tetrahydrate, A Primary Analytical Standard for Plutonium.	C. E. PIETRI
Some Aspects of Measurement of Oxygen to Metal Ratio in Solid Solutions of Uranium and Plutonium Dioxides.	J. L. DRUMMOND and V. M. SINCLAIR
Direct Volumetric Determination of Uranium or Plutonium in Nitric Acid Medium.	J. CORPEL
Ion-Exchange Separation of Actinides with Nitric Acid-Methanol and with EGTA.	J. HINES, M. WAHLGREN and F. LAWLESS
Ion-Exchange Purification of ^{147}Pm and its Separation from ^{241}Am with Diethylenetriaminepentaacetic Acid as Eluant.	P. B. ORR
Studies of Polymerisation of Quadrivalent Plutonium by Spectrophotometric Methods.	D. A. COSTANZO and R. E. BIGGERS
Determination of ^{137}Cs in Solutions of Irradiated UO_2 Fuel using Preformed Ammonium Molybdophosphate.	G. M. ALLISON and R. A. FERGUSON

Thursday 11 *October*

Morning—*Session on Use of Isotopes in Analytical Chemistry*

Radioactive Indicators in Analysis.	C. ROSENBLUM
Determination of Thorium and Alkaline-Earth Elements by Isotope Dilution.	S. A. REYNOLDS
Application of One-Step Radiometric Titration to Analysis of Aluminium Containing Silicates.	D. S. BERRY and B. F. SCOTT
Determination of Phosphorus in Uranium by Isotope Dilution Analysis.	F. W. LIMA and L. T. ATALLA
Applications of Radioisotopes in Polarography.	W. B. SCHAAP and E. WILDMAN
Some Problems Involved in Utilising Radioisotopic Tracers.	G. GOLDSTEIN
Use of Radioisotopes in Determination of Distribution Coefficients of Alkali Metals in an Organic Phosphate-Aqueous System.	R. J. KLETT and B. WILKINS, JR.

Atomic Absorption and X-Ray Spectroscopy Session

Atomic Absorption Spectroscopy—A Review.	P. T. GILBERT, JR.
An Atomic Absorption Tube for Use with an Atomiser-Burner: Application to Determination of Mercury.	C. FELDMAN and R. K. DHUMWAD
Applications of Atomic Absorption Spectrophotometry to Isotope Analysis.	W. SLAVIN
A Grating Monochromator.	W. KAYE
An X-Ray Emission Method for Determining Uranium and Plutonium in Binary and Ternary Mixtures.	O. MENIS, E. HALTEMAN and E. E. GARCIA

Analytical Techniques used in Evaluating High-Temperature Phase Equilibria· Application to the UO_2-ThO_2-O_2 System.	H. A. FRIEDMAN
Afternoon—*Mass Spectroscopy Session*	
Utilisation of a Spark-Source Mass Spectrograph for Analysis of Reactor Materials.	W. J. SEWALK and H. D. COOK
Investigation of Burnup Determinations on Highly Irradiated Fuels by Mass Spectrometric Methods.	H. D. COOK, C. J. RETTGER and W. J. SEWALK
A Safe Semiautomatic Fluorination System for Preparation of UF_6 Mass Spectrometer Samples.	J. K. REUSCH and R. D. OHLINGER
General Session	
Determination of Free Acid in an Organic Phase of Trilaurylamine.	A. CHESNE
Determination of Oxygen in Lithium.	R. J. JAWOROWSKI, J. R. POTTS and E. W. HOBART
Determination of Rubidium in Rubidium-Doped, Thalliated, Sodium Iodide Scintillation Crystal Using Sodium Tetraphenylboron.	K. J. JENSEN
Beryllium Determination as $Be_2P_2O_7$.	C. BAMBERGER and J. L. HUGUET
Dissolution of Irradiated, High-Fired, Refractory, Nuclear Materials.	H. KUBOTA and R. F. APPLE

Wednesday 31 *October–Saturday* 3 *November* 1962: **Ninth National Vacuum Symposium:** *American Vacuum Society.* Statler Hilton Hotel, Los Angeles, California (see *Talanta*, 1962, **9**, 406).

Monday–Thursday 20–30 *May* 1963: **International Symposium on Humidity and Moisture—Measurement and Control in Science and Industry:** *National Bureau of Standards, U.S. Weather Bureau, American Society of Heating, Refrigerating and Air Conditioning Engineers, Instrument Society of America* and *American Meteorological Society.* Washington D.C.

The symposium will review current progress and present the results of original research and development work on measurement and control of humidity and moisture in the physical, engineering, meteorological, agricultural and biological sciences.

Further details may be obtained from ARNOLD WEXLER, National Bureau of Standards, Washington 25, D.C.

Talanta, 1962, Vol. 9, p. 810. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Spectrophotometric study of *p*-nitrosodiphenylamine as a reagent for rhodium: JAMES R. STOKELY and WILLIAM D. JACOBS. (2 *July* 1962).

Triethylenetetraminehexa-acetic acid as a new volumetric reagent: RUDOLF PŘIBIL and VLADIMÍR VESELÝ. (2 *July* 1962).

Beobachtungen am Verbrennungsverlauf organischer Substanzen: E. PELL and H. MALISSA. (2 *July* 1962).

Precipitation of cadmium from homogeneous solution using 8-acetoxyquinoline: ROGER D. WHEALY and B. J. BLAND. (10 *July* 1962).

Differential coulometric analysis: A high precision technique and its application to the determination of dichromate by constant current generation of ferrous ion: R. G. MONK and G. C. GOODE. (13 *July* 1962).

Analytical applications of the flame emission spectra of lead and titanium: C. L. CHAKRABARTI, R. J. MAGEE and C. L. WILSON. (17 *July* 1962).

Spectrophotometric determination of the dissociation constant of the Woods reagent, 2-hydroxymethyl-6(2′-hydroxymethyl-5′-hydroxy-4′-pyrone-6′)pyranyl [3,2-B] pyran-4,8-dione: R. F. WILSON and G. W. LESTER. (17 *July* 1962).

4(2-Pyridylazo)resorcinol as a selective and sensitive spectrophotometric reagent for niobium(V): R. BELCHER, T. V. RAMAKRISHNA and T. S. WEST. (17 *July* 1962).

L'oxalate de *p*-dimethylaminoaniline dans la colorimétrie des aldehydes et des ceto-stéroides: MAURICE PESEZ et JAROSLAV BARTOS. (17 *July* 1962).

Some theoretical and practical problems in the use of organic reagents in chemical analysis—II: Effect of hydrogen bridge and donor π bond on the stability of transitional metal chelates of dioximes: K. BURGER and I. RUFF. (17 *July* 1962).

***p*-Thiocresol as a new reagent for technetium and rhenium:** M. AL-KAYSSI and R. J. MAGEE. (17 *July* 1962).

A study of the extraction and absorptiometric determination of titanium with 8-hydroxyquinoline: C. L. CHAKRABARTI, R. J. MAGEE and C. L. WILSON. (19 *July* 1962).

An investigation of the chelatometry of Cu(II) with ethylenediamine-N,N,N′,N′-tetra-*n*-propionic acid: I. P. SANDERSON and T. S. WEST. (19 *July* 1962).

Cation-exchange separation of scandium: HIROSHI HAMAGUCHI, ROKURO KURODA and KOREKAZU AOKI. (19 *July* 1962).

Voltammetry of silver in molten sodium nitrate–potassium nitrate: D. L. MANNING. (24 *July* 1962).

The chromatographic separation and determination of niobium, tantalum and titanium: I. MARTIN and R. J. MAGEE. (25 *July* 1962).

The iodometric estimation of tin: D. I. BOTHWELL and A. A. MOSS. (26 *July* 1962).

Talanta, 1962, Vol 9, pp 811 to 821 Pergamon Press Ltd. Printed in Northern Ireland

A CRITICAL EXAMINATION OF METHODS USED FOR THE DETERMINATION OF AVAILABLE OXYGEN IN HIGHER METAL OXIDES

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(*Received* 13 *June* 1961 *Accepted* 23 *May* 1962)

Summary—Careful examination of the Bunsen, oxalate, iodide and ferrous methods used in the determination of available oxygen in manganese and cobalt oxides has shown that the last three methods invariably give high results while the Bunsen method, when suitably modified, gives accurate results It is suggested that the discrepancy between the Bunsen and other methods is caused by an adsorbed monolayer of oxygen upon the surface of the oxides examined

INTRODUCTION

AVAILABLE oxygen (*i e.* the percentage of excess oxygen above that required by the lowest stable valency state) in certain metal oxides can be determined by at least five standard methods, none of which offers simultaneously the advantages of speed, accuracy, precision, and convenience of operation:—

(1) *Bunsen's method.* The sample is heated in concentrated hydrochloric acid and the liberated chlorine collected in potassium iodide. The resulting iodine is titrated with standard thiosulphate.

$$MnO_2 + 4H^+ + 2Cl^- \rightarrow Mn^{2+} + Cl_2 + 2H_2O.$$

(2) *Oxalate method.* The higher oxides are digested with a dilute sulphuric acid solution of excess sodium oxalate until decomposition is complete, *e.g.*

$$(COO)_2^{2-} + 6H^+ + Mn_2O_3 \rightarrow 2CO_2 + 2Mn^{2+} + 3H_2O$$

and the excess oxalate is back titrated with standard permanganate. The method is satisfactory for most mineral manganese oxides, but fails inexplicably with some.

(3) *Direct iodide method.* This method, which is applicable only to finely-ground chemically pure oxides containing cations which do not form insoluble iodides or sulphates, is based upon reactions of the type:

$$Mn_2O_3 + 2I^- + 6H^+ \rightarrow 2Mn^{2+} + 3H_2O + I_2$$

and the liberated iodine is titrated with standard thiosulphate.

(4) *Ferrous method.* The essential reaction is, for example:

$$2Fe^{2+} + MnO_2 + 4H^+ \rightarrow 2Fe^{3+} + Mn^{2+} + 2H_2O$$

followed by a back titration of excess ferrous ions with standard permanganate or, better, dichromate. The decomposition of the oxide, which must be performed at the boil under an inert atmosphere, is slow for low grade mineral oxides of manganese.

(5) *Arsenite method.* The oxide is heated with arsenite in dilute sulphuric acid solution:

$$AsO_3^{3-} + 6H^+ + Mn_3O_4 \rightarrow AsO_4^{3-} + 3Mn^{2+} + 3H_2O$$

and the excess arsenite back titrated with standard permanganate in the presence of iodate as catalyst.

These methods allow the determination of all higher valencies in the samples, provided that the reduction potentials are suitable. Hence, as an example, the determination of available oxygen in a pyrolusite specimen by the oxalate method gives a titre which is derived from the dioxide and any manganic or manganomanganic oxides which are almost certain to be present in the mineral. The reporting of the oxidising power, "available manganese," of manganese minerals as MnO_2 is therefore open to criticism.

Of the methods tested, the oxalate reduction is the most popular because of its simplicity of manipulation and reasonable accuracy, while the ferrous reduction is open to errors from air-oxidation and, in common with the direct iodide and arsenite methods, is less versatile in the determination of lower grade pyrolusites. The Bunsen chlorine evolution method has long been regarded as the referee method for higher oxides, but because of its relatively complex manipulation has not proved popular as a routine method.

Little regard has been paid to the accuracy of the methods: the reasons for choosing Bunsen's method as the most precise and accurate for referee purposes seem lost in antiquity, while only recently[1] has the oxalate method been investigated in any detail. It is difficult to judge the standards upon which any estimate of accuracy is or has been made in any of the methods.

In the present work an attempt has been made to compare the accuracy of the methods, and incidentally, to compare their precision and improve the techniques. The methods investigated were (1) Bunsen's method because of its supposed referee qualities, (2) the oxalate method because of its universal usage, (3) the iodide method because of its extraordinary simplicity in the determination of chemically prepared oxides, and (4) the ferrous method because of its use of chemically reversible systems. The arsenite method was not investigated because of its lack of versatility. Although most of the work was performed on manganese oxides, some results are reported on those of cobalt.

RESULTS AND DISCUSSION

(1) *Bunsen's method*

In using the apparatus and technique described in standard works,[2] it was found that, in comparison with the oxalate method and with reasonably pure standard samples of manganese dioxide and manganomanganic oxide, the chlorine evolution method gave results which were as much as 5% low in recovery of available oxygen. The design of the distillation apparatus was improved with particular regard to quantitative distillation and quantitative collection of the chlorine: thus the vapour path was shortened and made as free of obstruction and dead-gas pockets as was practicable, and the absorption was performed through a sintered glass plate. The final design of apparatus is shown in Fig. 2, but for the earlier investigations the small distillation flask was replaced with a similar 100-ml flask. In this apparatus rarely did the witness flask show evidence of ingress of chlorine and all of the available

chlorine was displaced into the first potassium iodide absorption flask in a reasonable time at a reasonable flow rate of carbon dioxide. Additions of pure sodium bicarbonate to the absorption solution in order to prevent excessively high hydrogen ion concentrations had little effect, and results were still low. (This practice became completely unnecessary when smaller volumes of acid were used for the decomposition.) These low results were ascribed to either or both the dissolution or reaction of chlorine in the water present in the still or the formation of complex chlorides of higher valency states of the metal concerned. Both of these effects should be reduced by decreasing the recommended volume of hydrochloric acid. Results for varying volumes and two concentrations of acid are shown in Fig. 1, based upon suitable weights of specimens of oxides of approximately known composition.

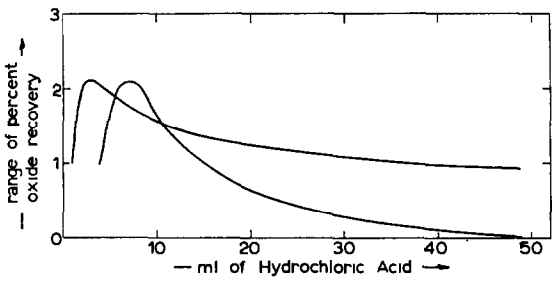


FIG. 1 —General shape of curves for the recovery of manganese and cobalt oxides with varying volumes of hydrochloric acid

It is evident that the volume of hydrochloric acid normally recommended (25–50 ml) is much too great and that with an optimum volume of acid, maximum recovery is obtained. This maximum is obtained at a volume which is barely twice that required for chemical equivalence, and at the same time, no high concentrations of hydrogen ions are introduced into the receiver and the blank experiments give negligible titres.

In an effort to reduce still further the quantity of water in the still, experiments were performed with mixtures of anhydrous phosphoric acid ("100% orthophosphoric acid") and dried sodium chloride instead of hydrochloric acid. However, even under optimum conditions, found to be 20 ml of phosphoric acid with 5·5 g of sodium chloride for 0·2–0·3 g of the various manganese or cobalt oxides, a maximum recovery of less than that obtained in the modified Bunsen's method was obtained on the same bulk samples (see Table 1).

TABLE I —ANALYTICAL RECOVERY OF MANGANESE OXIDES BY TWO MODIFICATIONS OF BUNSEN'S METHOD

Decomposition agent	Analytical recovery of manganese oxides, %		
	MnO_2	Mn_2O_3	Mn_3O_4
2 5 ml of 12*N* HCl	98 8	99 9	99 5
20 ml of H_3PO_4 + 5 5 g of NaCl	97 9	98 5	97 8

Considerable care was exercised in controlling the temperature of decomposition; although the maximum temperature was 160°, some dehydration of the orthophosphoric acid did occur, as evidenced by appreciable quantities of condensed water in the still head. At the same time it was noted that the residue in the still had a strong

purple colour, similar to that of the manganic-pyrophosphate complex. Complex formation of an intermediate valency, present even in small quantities, with a condensed phosphoric acid product would lead to the low results found in practice.

Similar complex formation may well account for the low results obtained with the classical Bunsen's method, in that the liquid remaining after the distillation from any volume of hydrochloric acid often had a distinct greenish-purple colour. This was particularly obvious when the optimum (2·5 ml) volume of acid was used, but could be discharged by evaporating the liquid just to dryness, when it did not reappear on dissolving the residue in water, or by adding sodium thiosulphate. In all of the cases tested no further detectable chlorine was evolved, or the quantity of 0·05*N* thiosulphate required was less than 1 drop.

The method appeared to be applicable to lead oxides, giving results for triplumbic tetroxide which were in reasonable agreement with the calculated figures and with a standard deviation similar to the results for manganese oxides. However, none of the other methods could be applied to lead oxides and comparisons were, therefore, made impossible.

(2) *Oxalate method*

The standard technique was used, but the approximately 0·1*N* potassium permanganate was standardised against sodium oxalate solutions which had been treated in a manner identical to the determination mixtures. The method failed for lead oxides, even when other acids were used instead of sulphuric acid.

(3) *Direct iodide method*

The sample (0·2–0·5 g) was dissolved in 50 ml of dilute (1:20 or 1:10) sulphuric acid in the presence of 4–5 g of potassium iodide while the mixture was cooled in ice. For pure oxides of manganese the reaction is fairly rapid, but much slower for those of cobalt; most minerals and lead oxides, even when finely ground, are largely insoluble.

Results for analyses by this method are highly reproducible and in remarkably good agreement with those of the oxalate method, but slightly higher than those of the modified Bunsen's method. To check whether this discrepancy was caused by the presence of oxygen in the solutions used, experiments were run in a still nitrogen atmosphere after degassing the solutions with nitrogen. In fact, degassing with nitrogen has little effect save the reduction of the blank to a negligible figure. On the assumption that Bunsen's method gives the correct results, these slightly high figures from the direct iodide method may be caused by either catalytic decomposition of iodide by the surface of the oxides, or, more likely, any adsorbed oxygen on the surface is reduced by the iodide ions and the resulting iodine titre is then ascribed to "available oxygen." This hypothesis is in accord with the fact that maximum development of the triodo ion's colour is almost instantaneous when a sample of manganous or cobaltous oxide is added to a dilute sulphuric acid solution of potassium iodide and the more finely divided samples of the oxides gave higher available oxygen figures.

(4) *Ferrous method*

This method has already been shown[1] to give results somewhat lower than those of the oxalate method. On two high grade pyrolusites the results shown in Table II by the modified Bunsen, oxalate and ferrous methods were obtained. Potassium dichromate was used as primary standard for the latter method.

TABLE II —COMPARISON OF RESULTS BY THE BUNSEN, OXALATE AND FERROUS METHODS

Method	Available oxygen as MnO_2, %	
	Sample 1	Sample 2
Oxalate	88 8	83 9
Ferrous	88 2	83 8
Bunsen	88 0	83 6

Results obtained on samples of manganese dioxide and manganomanganic oxide show that results are similarly intermediate between the Bunsen and oxalate methods.

Comparison of results between methods and with standards

Results for various samples of manganese and cobalt oxides carefully prepared according to the literature,[4,5] are presented in Table III.

Ignoring manganese dioxide samples 1, 2, 6, 7a and 7b, which are discussed later, it is quite clear from these data that the oxide, oxalate and ferrous methods give results which are reproducible and in close agreement. In addition, the methods digress from the modified Bunsen's method by a positive value of 0·15–0·25%, while the ferrous method tends to give intermediate results. Obviously the composition of different preparations of the oxides is so variable that it is not easy to decide, by comparison with calculated available oxygen values, which is the most accurate method. However, for routine purposes it is clear that any of the four methods would be satisfactory provided that simple ores were under investigation.

The preparation of a really good standard of a manganese or cobalt oxide presents a remarkably difficult problem. There are no standards, except electrolytic manganese metal, from which to make a compound of sufficient quality for this work. Ignition of the metal to, say approximately manganomanganic oxide, requires an excessively long time during which volatilisation losses could be serious, while dissolution of the sample, say in acid, followed by ignition to an oxide has so many possible sources of loss that it would be open to criticism. In any case, the formula of the product could not be assumed to be correct with exactitude, because workers who assigned formulae to the various oxides must have used analytical procedures which had not been subjected to the present intensive criticism and took no account of non-stoicheiometry. Hence, the oxidation would have to be followed gravimetrically and all traces of manganese metal removed from the product. However, oxidation of electrolytic manganese in platinum and alumina crucibles under air at 1000° was attempted, with mean results shown in Table IV.

Although the gain of available oxygen by weight agrees more closely with Bunsen's method than with the oxalate method, more cognisance should be taken of the agreement of the Bunsen method with the calculated available oxygen content of trimanganic tetroxide. This agreement is also found in other good samples of this oxide (see Samples 1, 2, 3, 4 and 6 in Table III). Trimanganic tetroxide is said to be the "most stable" oxide of manganese and to display the least non-stoicheiometry of the series.

Another approach to the problem lies in the preparation of pure manganous oxide, MnO. This oxide can be prepared[3] by reduction of the higher oxides with pure

TABLE III—PERCENTAGE OF AVAILABLE OXYGEN IN MANGANESE OXIDES BY FOUR METHODS

	Manganese dioxide (Calculated [0] = 18 40%)				Manganic oxide (Calculated [0] = 10 13%)				Trimanganic tetroxide (Calculated [0] = 6 99%)			
Method	Bunsen	Iodide	Oxalate	Ferrous	Bunsen	Iodide	Oxalate	Ferrous	Bunsen	Iodide	Oxalate	Ferrous
Sample												
1	$18\ 42_6 \pm 0\ 02_1$	$18\ 20_9 \pm 0\ 01_4$	$18\ 21_1 \pm 0\ 01_4$	—	$9\ 52_5$	$9\ 62_8$	$9\ 66_3$	—	$6\ 88_3$	$6\ 99_3$	$7\ 03_3$	—
2	—	—	$18\ 08_8 \pm 0\ 02_5$	$18\ 00_9 \pm 0\ 01_1$	$9\ 80_7$	$9\ 92_0$	$9\ 96_7$	—	$6\ 89_3$	$7\ 02_0$	$7\ 05_7$	—
3	—	—	—	—	$9\ 89_3$	$10\ 02_7$	$10\ 05_3$	—	$6\ 91_7$	$7\ 05_0$	$7\ 07_7$	—
4	—	—	—	—	$9\ 97_3$	$10\ 09_3$	$10\ 11_0$	—	$6\ 97_8$	$7\ 10_3$	$7\ 12_2$	—
5	—	—	—	—	—	—	—	—	—	—	$7\ 29_1 \pm 0\ 02_4$	$7\ 07_4 \pm 0\ 01_1$
6	$18\ 29_8 \pm 0\ 02_0$	$18\ 17_5 \pm 0\ 02_0$	$18\ 20 \pm 0\ 02_6$	$18\ 14_0 \pm 0\ 02_8$	$10\ 09_6$	$10\ 27_8$	$10\ 31_3$	$10\ 12_0$	$6\ 96_7$	$7\ 06_5$	$7\ 14_4$	$6\ 97_7$
7(a)	18 38	18 28	18 26	18 27								
(b)	18 36	—	18 29	—								
(c)	18 22	18 26	18 27	18 23								
			Standard deviation of a single result		$\pm 0\ 02_6$	$\pm 0\ 02_4$	$\pm 0\ 02_3$	—	$\pm 0\ 02_0$	$\pm 0\ 02_2$	$\pm 0\ 01_9$	

TABLE IV —AVAILABLE OXYGEN IN MANGANESE OXIDE OBTAINED BY AIR-OXIDATION OF ELECTROLYTIC MANGANESE

Sample	Available oxygen		
	By weight, %	By Bunsen, %	By oxalate, %
1	6 90	6 94	7 09
2	6 81	6 93	7 13
3	6 80	6 96	7 24

dry hydrogen at 1100–1600°. Of the oxides, the manganic at 1200° appeared to be the best starting material in giving the greenest product which appeared to oxidise (through a brownish-green) extremely slowly. Use of other oxides and lower temperatures gave more finely divided products which oxidised much more rapidly. Examination of the product and the similar cobaltous oxide prepared by heating cobalto-cobaltic oxide in pure dry nitrogen, by the three methods gave the results listed in Table V, in which samples 3 and 4 were the best preparations.

TABLE V —PERCENTAGE AVAILABLE OXYGEN IN MANGANOUS AND COBALTOUS OXIDES

	Manganous oxide				Cobaltous oxide	
Method	Bunsen	Iodide	Oxalate	Ferrous	Bunsen	Oxalate
1	Nil	0 053	0 057	—	Nil	0 20
2	Nil	0 044	0 047	—	Nil	0 16
3	Nil	0·036	0 033	0 021	Nil	0 11
4	Nil	0·028	0 026	—	Nil	0 10
5	—	—	0·076	0 041	—	—

Although the oxalate and iodide methods give results higher than those of the Bunsen method, the quantity by which they are high (0·026–057 and 0·10–0·20, respectively) is far less than the difference obtained on the higher oxides. Hence, if oxygen is added to the manganous oxide, the increase in weight (*i.e.* available oxygen) measured gravimetrically can be truly compared with the available oxygen determined titrimetrically.

Weighed samples of manganous and cobaltous oxide specimens were heated at 750° in a stream of pure dry oxygen for 18 hr, cooled in the gas, and the resulting black oxides, corresponding approximately to manganic oxide and cobalto-cobaltic oxide, were reweighed. The increase in weight was compared with available oxygen determinations obtained by the three titrimetric methods.

The differences between the gravimetrically measured gain and the results obtained by the Bunsen and oxalate methods obtained from a large number of determinations are shown in Table VI with the corresponding standard deviations.

TABLE VI —DIFFERENCES BETWEEN DETERMINATIONS OF AVAILABLE OXYGEN BY WEIGHT AND BY CHEMICAL MEANS

	Manganese Oxide			Cobalt Oxide	
Method	Bunsen	Iodide	Oxalate	Bunsen	Oxalate
Mean Difference	$-0\ 00_4 \pm 0\ 03_8$	$+0\ 29_2 \pm 0\ 05_3$	$+0\ 23_3 \pm 0\ 02_3$	$-0\ 03_0 \pm 0\ 01_3$	$+0\ 28 \pm 0\ 06_5$

The differences are clearly significant and according to this test, the modified Bunsen method can be taken as accurate *and* precise whereas the oxalate and direct iodide methods, while being precise, suffer from a positive constant error of approximately 0·25%. This is in agreement with the findings of the several analyses performed on other oxide specimens; such a large discrepancy is far greater than that from any unknown quantity of available oxygen in the manganous or cobaltous oxides, this being a maximum of 0·05 and 0·15%, respectively, determined by any method.

Qualitative inspection of the oxide samples indicated that average particle sizes varied in the order manganous oxide > cobaltous oxide > manganese dioxide, manganic oxide, manganomanganic oxide, and for manganous oxide specimens (Table V), samples 4 > 3 > 2 > 1. Coupled with the observation that, in the iodide method, development of the triodo ion's colour is virtually complete in the first few moments of bringing the reagents together, this correlation between particle size, and therefore area, and discrepancy between the results of the various analytical methods indicates that the cause lies in a surface phenomenon. Consequently, experiments were conducted using the Brunauer-Emmett-Teller adsorption isotherm[7] in order to evaluate the surface area of some of the oxides. Results are given in Table VII, together with the area occupied by a monolayer of oxygen atoms calculated from the excess available oxygen obtained as a difference between the modified Bunsen's and oxalate methods.

TABLE VII —SURFACE AREA OF MANGANESE OXIDES

Sample	Oxygen difference, %	Specific surface area, cm^2g^{-1}	
		From excess oxygen	From B E T isotherm
Manganous oxide	0·030	$1\,6 \times 10^3$	$1\,7 \times 10^3$
Manganomanganic oxide	$0\,15_5$	$8\,3 \times 10^3$	$8\,5 \times 10^3$
Manganic oxide	$0\,17_7$	$7\,4 \times 10^3$	$7\,3 \times 10^3$

Because the estimated error in all of the surface area measurements is expected to be approximately $\pm 0{\cdot}4 \times 10^3$ cm^2 g^{-1}, the correlation between the results is extremely close and it is reasonable to suppose that these oxides, as prepared, have an adsorbed monolayer of oxygen atoms. Furthermore, because this oxygen is available for reduction only by certain reducing agents, the mechanism is likely to be chemical rather than physical adsorption.

Against this it may be argued that the difference between methods for any given oxide are remarkable constant while among several preparations it is unlikely that the same surface area is consistently obtained. Moreover, the agreement between the Bunsen method and the addition of oxygen measured by weight (Table VI) and the corresponding high results for the oxalate and iodide methods is not in accord with the hypothesis

The high results obtained with the Bunsen method for manganese dioxide samples 1, 6, 7(a) and 7(b) are from the presence of an impurity, probably manganous nitrate, in these samples. A specimen (2 5 g) of manganese dioxide prepared by a published method[4] was examined thermogravimetrically under one atmosphere of dry oxygen. the sample began to lose weight at 425°, and at 510° reached constant weight within 5 hr. Above 520° decomposition to manganic oxide commenced. A more finely ground sample (1·4 g) behaved similarly but constant weight was reached within 1 hr

at 510°. The weight loss corresponds approximately to a 0·74% content of manganese nitrate which would account for 0·14% of available oxygen as determined by the Bunsen method, but would not interfere in any of the other methods. The presence of oxynitrogen ions was demonstrated qualitatively in the original sample, but could not be detected in samples heated in oxygen at 510° for several hr. It was also observed that after the last treatment the finely ground samples gained weight on cooling in dry oxygen, but coarser specimens did not; however, the weight changes were so small that they could not be measured with any reasonable degree of accuracy. Results of these experiments are given in Table VIII

TABLE VIII

Sample	Available oxygen, %		Loss on heating to 510° in dry oxygen	Gain on cooling in dry oxygen
	Bunsen	Oxalate		
7(a) As prepared[4]	18 38	18 26	0 37%(≡0 14%[O])	Nil
7(b) After grinding and heating to 300° for 72hr	18 36	18 29	0 34%(≡0 12%[O])	~0 05%
7(c) After grinding and then heating to 510° in O_2	18 22	18 27	—	—

It is clear that the earlier samples of manganese dioxide were unsuitable for comparison purposes, although the statistical data obtained from them is satisfactory.

CONCLUSIONS

It is evident from the results that the four methods investigated are very reproducible on the samples examined. The modified Bunsen's method appears to give the most accurate results, while those of the ferrous, oxalate and direct iodide are consistently high. The positive error is probably caused by simultaneous oxidation of the oxalate (E_0, — 0·49V), ferrous (E_0, 0·77) and iodide (E_0, 0·55), which are in direct contact with the sample, by adsorbed oxygen on the surface of the oxide. The more positive standard electrode potential of chloride (E_0, 1·36) used in the Bunsen method, presumably does not allow reaction with this adsorbed oxygen. It is also possible that formation of oxalate and iodide complexes of tervalent manganese and cobalt could also contribute to the high results of the oxalate and direct iodide methods. For pure oxides, but not minerals, the results of the ferrous method, in which complex ion formation is unlikely, are barely significantly different from those of the iodide and oxalate methods but the trend is in accord with this suggestion.

For minerals the oxalate results are in positive error by the greatest quantity; besides air-decomposition of the oxalate, suggested by other workers,[1] it is possible that small quantities of oxalate complexes of other cations are formed or other reducible cations are included in the results nominally given for "available oxygen".

Nevertheless, for routine purposes on suitable minerals and ores, the oxalate and certainly the ferrous methods are adequate: only in referee analyses of oxides does the difference between the methods become significant. Clearly, for accurate work on oxides, considerable care must be exercised over sampling procedures in order that the proportions of all particle sizes and therefore surface areas, are represented in the weighted sample.

EXPERIMENTAL

Preparation of oxides

Manganese and cobalt oxides were prepared by standard methods (MnO_2,[4] Mn_2O_3,[5] Mn_3O_4,[5] Co_2O_3,[5] Co_3O_4[5]). In addition, at the end of each preparation, each sample was finely ground, and reheated at the prescribed temperature for a further period of 4 hr It was ultimately discovered that, because of included nitrate ions, it was necessary to heat manganese dioxide specimens in dry oxygen at 510° for several hr before a suitable sample was obtained As much as 0 7% of impurity, presumably manganese^{II} nitrate, is present in the dioxide prepared by published methods

Manganous oxide[3] was prepared by passing a stream of oxygen-free hydrogen which had been dried over silica gel and anhydrous magnesium perchlorate over the sample of a higher oxide of manganese heated at 1200° for 8–10 hr The oxide was cooled in hydrogen and analysed as soon after reduction as possible The most massive and brightest green samples were obtained from manganic oxide, and these preserved their low available oxygen content for more than 3 years Cobaltous oxide[6] was prepared similarly, the decomposition of the higher oxides being achieved with oxygen-free nitrogen which had been dried over silica gel and magnesium perchlorate and passed over copper turnings at 500–600°. Reduction of cobaltocobaltic oxide at 1100° gave the best products

The intermediate oxides of manganese and cobalt were prepared by heating manganous or cobaltous oxide at 750–800° in a stream of pure dry oxygen for 18–24 hr

Apparatus

Weighings All weighings were performed on balances sufficiently precise to give a relative error of less than 0 05% Calibrated weights were used throughout

Thermogravimetric analyses The thermogravimetry was performed on a Stanton Thermobalance modified to allow sensitive low temperature control and provision of controlled gas atmospheres round the sample

Titrations All titrations were carried out on the same calibrated Grade A burette and, as far as possible, all titres were arranged to fall between 45 and 50 ml The same drainage time was employed throughout The limits of reading the burette were an estimated 0·02 ml and titrations were performed to fractions of 1 drop

Methods

Oxalate method. The determinations were performed in the usual manner The samples were heated with the dilute (1 10) sulphuric acid solution of sodium oxalate at 95° and the sodium oxalate standards were treated similarly, no inert gas atmospheres were deliberately used

Ferrous method Standard procedures were adopted using dilute (1 10) sulphuric acid as solvent and a carbon dioxide atmosphere Dried potassium dichromate was used as primary standard

Direct iodide method The samples (0 2–0 5 g) were dissolved in ice-cooled dilute (1 20 or 1 10) sulphuric acid containing 4–5 g of potassium iodide, the solutions were magnetically stirred, if necessary For manganese oxides, decomposition was complete within 60 min The solutions were titrated with standardised 0·1*N* sodium thiosulphate Allowance was made for a blank

Modified Bunsen's method The final apparatus is shown in Fig 2 Noteworthy points of design are its extremely small still (S), smooth vapour path (including capillary-tipped tap funnel, T) and efficient chlorine absorption system (R_1 and R_2) Lubrication of joints was with "Fluorube W" grease

Place 50 ml of 20% potassium iodide in the first receiving flask (R_1) and 25 ml in the second flask (R_2) and surround R_1 and R_2 with ice-water Into the oven-dried distillation flask place 0 2–0·5 g of sample and assemble the apparatus With the aid of gentle suction introduce 2 5 ml of concentrated (36% w/w) hydrochloric acid into the still via the small tap funnel Start the moist carbon dioxide stream at 60–80 ml/min, disconnect the suction line, and gently heat the flask over a small hooded flame until the sample has completely dissolved Increase the flame so that the solution evaporates just to dryness The overall heating time usually occupies 30–45 min, but continue the passage of carbon dioxide to a total of 60 min With the gas still flowing, disconnect R_1 and wash down the outside and inside of the delivery tube (D) with distilled water using gas pressure to assist the emptying of the tube Immediately titrate the liberated iodine with standard sodium thiosulphate. The quantity of free iodine in the witness flask and in a blank run should both be less than 1 drop of titrant

The sodium thiosulphate was standardised against weighed samples of dried potassium iodate which gave identical figures to those using pure copper No indicator was used in the standardisation or determinations because the change from yellow to colourless at the end-point was extremely sharp. Standardisation of the thiosulphate was performed daily during this work

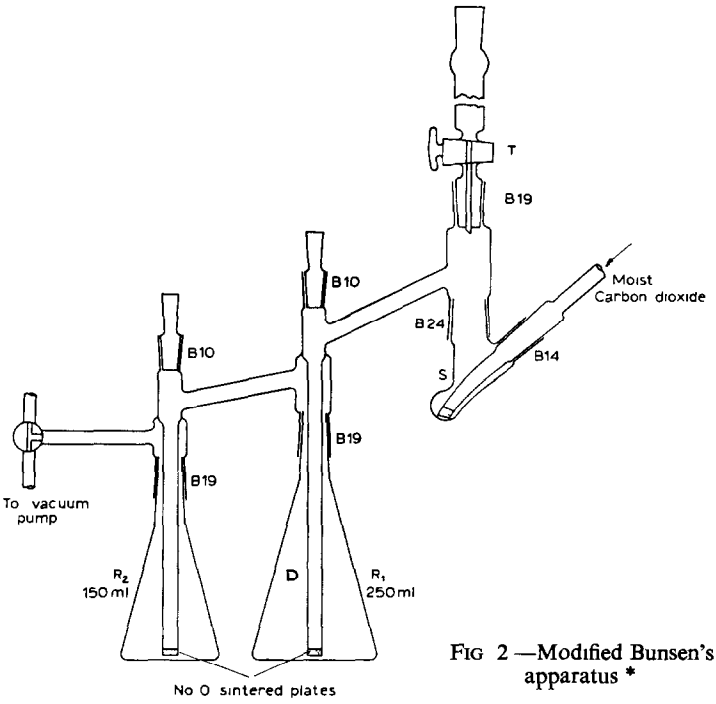


FIG 2—Modified Bunsen's apparatus *

Acknowledgement—Thanks are due to Dr A P Prosser for facilities to perform the Brunauer-Emmett-Teller test

Zusammenfassung—Folgende Methoden zur Bestimmung des aktiven Sauerstoffes in Mangan- und Cobaltoxyden wurden kritisch verglichen. Bunsen, Oxalat- Iodid- und Ferroeisenmethode Es wurde gefunden, dass die letzteren drei Methoden zu hohe Resultate liefern, wahrend die Ergebnisse nach Bunsen (geeignet mofifiziert) korrekt sind Der Unterschied der Ergebnisse wird auf eine monomolekulare Sauerstoffschichte an der Oberflache des Oxydes zuruckgefuhrt.

Résumé—L'examen soigné des méthodes de BUNSEN, de l'oxalate, de l'iodure et du fer ferreux utilisées dans le dosage de l'oxygène activé présent dans les oxydes de manganèse et de cobalt a montré que les trois dernières méthodes donnaient invariablement des résultats élevés, cependant que la méthode de BUNSEN, modifiée convenablement, donne des résultats précis La différence entre la méthode de BUNSEN et les autres méthodes est attribuée à une couche monomoléculaire d'oxygène adsorbé à la surface des oxydes examinés

REFERENCES

[1] M J Katz, R C Clarke and N F Nye, *Analyt Chem*, 1956, **28**, 507
[2] Scott's *Standard Methods of Chemical Analysis*, edited by N H. Furman 5th Ed, 1939, p 675; A I. Vogel, *A Textbook of Quantitative Inorganic Analysis* Longmans, Green & Co, London, 2nd Ed, 1951, p 345
[3] E G King, *J Amer Chem Soc*, 1952, **74**, 4446 M W Davies and F D Richardson, *Trans Faraday Soc*, 1959, **55**, 604
[4] K H Maxwell and H R Thirsk, *J Chem Soc.*, 1955, 4054
[5] N. V Sidgwick, *Chemical Elements and their Compounds* Oxford University Press, 1951, Vol II, p 1276
[6] R E Carter and F D. Richardson, *J Metals*, 1954, 1244
[7] S Brunauer, P H Emmett and E Teller, *J. Amer Chem Soc.*, 1938, **60**, 309.

* There is also a No 0 sintered plate at the inner end of the CO_2 inlet tube.

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REACTION OF CADMIUM WITH OXINE

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Summary—The stepwise reaction of cadmium with oxine has been studied and equilibrium constants calculated by polarographic and gravimetric methods

INTRODUCTION

IN the course of other work it was necessary to know the specific equilibrium constant for each step of the reaction of cadmium with the oxine (8-hydroxyquinoline) anion:

$$Cd^{2+} + Ox^- \rightarrow Cd(Ox)^+$$

and

$$Cd(Ox)^+ + Ox^- \rightarrow Cd(Ox)_2$$

where

$$K' = \frac{A_{Cd(Ox)+}}{A_{Cd^{2+}} A_{Ox-}} \quad (1)^*$$

$$\text{and } K'' = \frac{1}{A_{Cd(Ox)^+} A_{Ox-}} \quad (2)^*$$

We have measured the equilibrium constants K′ and K″. The measurements were carried out at an ionic strength of 1·00, temperature of 25° and initial pH of 6

EXPERIMENTAL

Reagents

Oxine Baker reagent grade oxine was purified by two recrystallisations from alcohol solution

Buffer A potassium acid phthalate-sodium hydroxide buffer system was used as suggested by Clark and Lubs

Cadmium chloride Dissolved in de-ionised water and standardised by two methods (1) titration with EDTA using Eriochrome Black T indicator, and (2) gravimetrically using the ethyl ester of oxine for homogeneous precipitation

Potassium chloride Reagent grade material was dried at 300° for 48 hr before weighing

Equilibrium measurements

The solutions were prepared and allowed to stand 72 hr before measurements were made Glass stoppered bottles were used to prevent evaporation

Two sets of solutions were prepared, each set having four samples to be used for gravimetric determination of $Cd(Ox)_2$ and one sample for polarographic determination of Cd^{2+}. The samples were mixed as follows: 20 00 ml of buffer solution, 20 00 ml of 2 400*N* potassium chloride, 5 00 ml of 0 1010*M* Cd^{2+} and 5 00 ml of oxine in alcohol Each set of solutions had a different ratio of Cd^{2+} to oxine initially as follows

Set	Ratio of $[Cd^{2+}]$ [Oxine]	$[Oxine]_{initially}$
A	1 2	0 0200
B	1 1½	0 0150

* Although equations (1), (2), (4) and (5) are expressed in activities, the calculations were actually made using concentrations, assuming concentrations to be equal to activities

The average weight of precipitate was obtained for each set The precipitate was weighed as $Cd(Ox)_2$ after drying to constant weight at 120–130°

The Cd^{2+} concentration for each set was determined polarographically using a Sargent Polarograph Model XXI in connection with a Leeds Northrup dropping mercury electrode which has a constant temperature bath and air tight sample container The pH of each solution was measured at equilibrium

RESULTS

The following values were obtained

$$K' = 5\,9 \times 10^{7} \pm 0\,5 \times 10^{7}$$
$$K'' = 4\,0 \times 10^{11} \pm 0{\cdot}3 \times 10^{11}$$
$$Ksp = 4\,2 \times 10^{-20} \pm 0\,30 \times 10^{-20}$$

CALCULATIONS

The initial concentration of Cd^{2+} is known and the weight of $Cd(Ox)_2$ and concentration of Cd^{2+} are measured at equilibrium. Therefore the concentration of $Cd(Ox)^{+}$ can be calculated using the following equation·

$$[Cd(Ox)^{+}] = [Cd^{2+}]_{initially} - \left\{[Cd^{2+}]_{equil} + \frac{\text{Wt. ppt.} \times 20}{400{\cdot}7}\right\} \tag{3}$$

This gives values for all forms of cadmium assumed to be present in the solution.*

The $[Ox^{-}]$ remains to be determined. Nasanen, Lumme and Mukula[1] have calculated the two ionisation constants of oxine at various ionic strengths. For a ionic strength of unity they give the following values:

$$K_1 = 6{\cdot}839 \times 10^{-6} \text{ and } K_2 = 2{\cdot}624 \times 10^{-10}$$

where

$$K_1 = \frac{A_{H^+}\, A_{HOx}}{A_{H_2Ox^+}} \tag{4}$$

and

$$K_2 = \frac{A_{H^+}\, A_{Ox^-}}{A_{HOx}} \tag{5}$$

Using the equation:

$$\text{Total Oxine} = [Ox^{-}] + [HOx] + [H_2Ox^{+}] \tag{6}$$

the concentration of each species can be expressed as a function of K_1, K_2 and pH, for example·

$$\frac{[Ox^{-}]}{\text{Total Oxine}} = \frac{K_1K_2}{[H^{+}]^2 + K_1[H^{+}] + K_1K_2} \tag{7}$$

Fig. 1 is a plot of the percentage of each of these species from pH 3 to 12. This indicates that all three species are present in this pH range.

The equilibrium concentration of oxine can be calculated as follows·

$$[\text{Total Oxine}]_{equil} = [\text{Oxine}]_{initially} - \left\{[Cd(Ox)^{+}] + \frac{2 \times \text{wt. ppt.} \times 20}{400{\cdot}7}\right\} \tag{8}$$

Now using $[\text{Total Oxine}]_{equil}$ and pH of the solution at equilibrium in equation (7) gives $[Ox^{-}]$.

* The amount of $Cd(Ox)_2$ dissolved, but un-ionised, in the solution is ignored No method could be devised to measure this amount, but it is believed from this work and from a hydrolysis study that it is quite small

This completes calculations for all concentrations to be used in equations (1) and (2), giving K′ and K″, respectively.

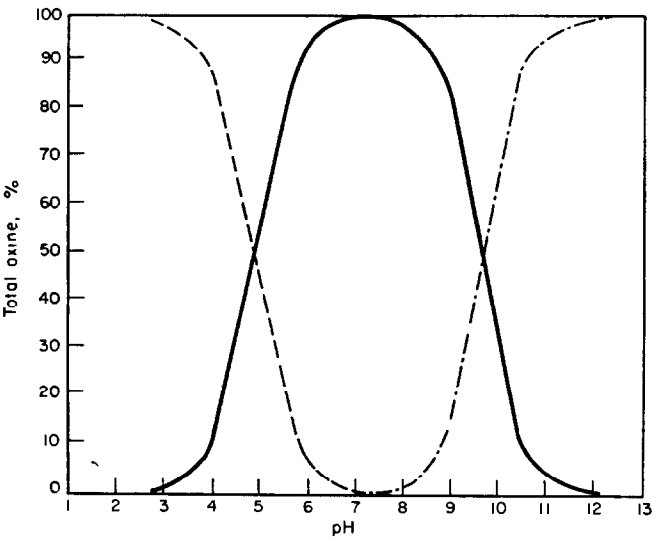


FIG 1 ——— HOx, - - - H_2Ox^+, —·— Ox^-.

The various concentrations of ions and weight of $Cd(Ox)_2$ in equilibrium solutions are as follows.

TABLE I

Set	$[Cd^{++}] \times 10^3$	$[Cd(Ox)^+] \times 10^3$	pH	$[Ox^-] \times 10^9$	$Cd(Ox)^{2g}$,
A	1·30 ± 0 03	1·00 ± 0·03	4 65 ± 0 02	9 6 ± 0·1	0 1555 ± 0 0038
B	3·00 ± 0 05	0 40 ± 0 02	4 67 ± 0·02	3 55 ± 0 05	0·1343 ± 0 0006

From these data K_{sp} can also be calculated:

$$K_{sp} = \frac{1}{K'K''} = \frac{1}{(5{\cdot}9 \times 10^7)(4{\cdot}0 \times 10^{11})} = 4{\cdot}2 \times 10^{-20} \pm 0{\cdot}2 \times 10^{-20}.$$

DISCUSSION

This method gives a relatively simple procedure for calculating the equilibrium constants and solubility products for bivalent metal oxinates. It can be used where the methods of spectrophotometry and potentiometry might not apply.

Nasanen and Penttinen[2] reported a value of $6{\cdot}03 \times 10^7$ for K′ which agrees very well with our value of $5{\cdot}9 \times 10^7$. Also, our value of $4{\cdot}2 \times 10^{-20}$ for K_{sp} is in fair agreement with their value of $3{\cdot}72 \times 10^{-21}$.

Johnston and Freiser[3] have studied the stability of metal oxinates and found the solubility product of $Cd(Ox)_2$ to be $3\ 16 \times 10^{-9}$ in a 50% dioxane-water solution at 25°. They did not consider the stepwise reaction of oxine with the metal ions and the various species of oxine present in solution. Their data cannot be extrapolated to aqueous solutions.

Zusammenfassung—Die stufenweise Reaktion von Cadmium mit Oxin wurde studiert und die Gleichgewichtskonstanten mittels polarographischer und gravimetrischer Methoden ermittelt

Résumé—Les auteurs ont étudié la réaction par paliers du cadmium avec l'oxine (8-hydroxyquinoléine) et calculé les constantes d'équilibre par des méthodes polarographiques et gravimétriques

REFERENCES

[1] R Nasanen, P Lumme and A L Mukula, *Acta Chem Scand*, 1951, **5**, 1199
[2] R Nasanen and U Penttinen, *ibid*, 1952, **6**, 837
[3] W D Johnston and Henry Freiser, *J Amer Chem Soc*, 1952, **74**, 5239

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DETERMINATION OF ANTIMONY IN LEAD BY NEUTRON-ACTIVATION ANALYSIS

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Summary—Activation analysis of antimony in lead has been studied in the concentration range of 1–0 03% Gold is used as a standard so as to avoid self-shielding problems of the antimony standard The proposed technique is possible by making use of net photospectra and computing the antimony content directly from the ratio of the 0 40- and 0 56-gamma peaks of ^{198}Au and ^{122}Sb

ACTIVATION analysis is not only a valuable tool for the determination of traces but it can also be successfully applied as a non-destructive technique for the determination of minor constituents, the accuracy of the results comparing favourably with other analytical methods.[1,2,3,4]

Activation analysis of traces of antimony has been studied by numerous workers as is apparent from the recent survey of Bock-Werthmann and Schulze [5] The present work deals with the non-destructive determination of antimony in lead by gamma spectrometry using gold as a reference standard.

Nuclear data

Natural antimony consists of two stable species, ^{121}Sb and ^{123}Sb, which can give rise to a number of radioisotopes by neutron irradiation as given in Table I.

TABLE I —NUCLEAR PROPERTIES OF ANTIMONY ISOTOPES

Stable isotope	Occurrence, %	Activation cross-section, *barn*	Isotope formed	Half life	Radiation and energy, *Mev*
^{121}Sb	57 25	3 7	^{122}Sb	2 8 day	β^- 0 740, 0 900, 1 40 1 97 γ 0 566; 0 686; 1 137, 1·256
		1 3	^{122m}Sb	3 5 min	I T e^- 0 059 γ 0 060; 0 075
^{123}Sb	42 75	1 1	^{124}Sb	61 day	β^- 0 240, 0 610; 0 966, 1 60, 2 32 γ 0 603; 0 641, 0 716, 1 68, 2 09
		0 013	^{124m}Sb	1 3 min	I T $e^-(\gamma)$0 012
		0 013	^{124m}Sb	21 min	I T $e^-(\gamma)$0 018

From Table I it appears that ^{122m}Sb, ^{122}Sb and ^{124}Sb can be used for activation purposes because they are formed in sufficiently large amounts to make accurate gamma spectrometric measurements possible. The half life of ^{122m}Sb is, however,

* Research fellow I I K.W.

very short so that measurement immediately after the end of the irradiation is required, whereas ^{124}Sb has a long half life and necessitates long irradiation periods to induce sufficiently large activities. Consequently, ^{122}Sb was chosen for measurement. The decay scheme and gamma spectrum of ^{122}Sb are given in Fig. 1.

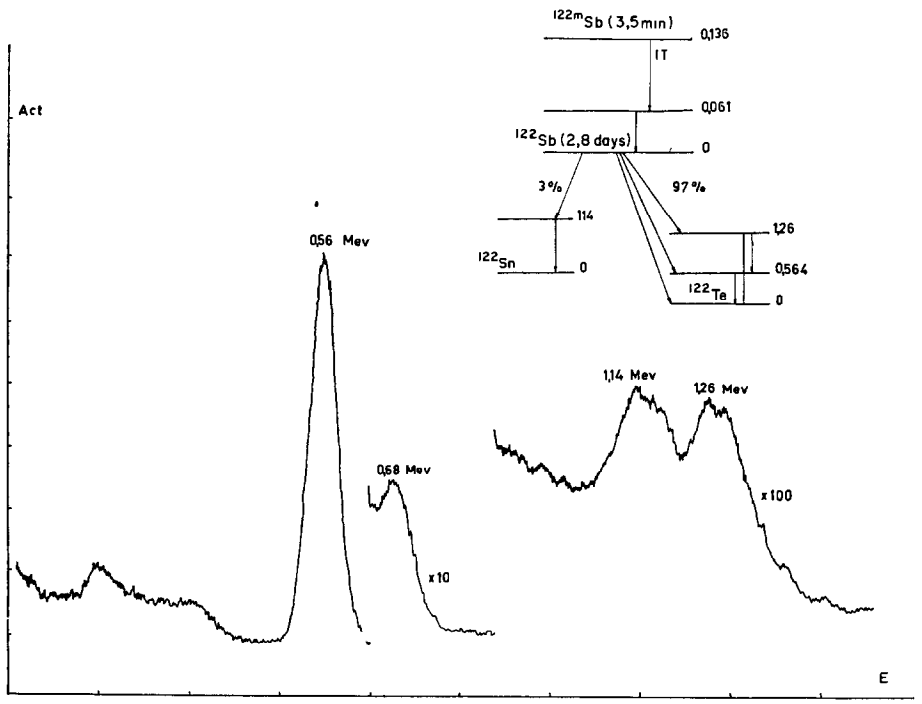


FIG 1—Decay scheme and gamma spectrum of ^{122}Sb.

Interfering activities

Because the activation cross-sections of the natural lead isotopes ^{206}Pb and ^{208}Pb are very small (0·026 and 0·0006 barn), the activity induced in the matrix is completely negligible. A number of other elements, occurring either as minor constituents or as traces, can, however, interfere with the determination of antimony as is apparent from Table II. These interferences can be minimised by restricting the measurement of ^{122}Sb to the 0·56-MeV gamma peak only. In this case the interference will be limited to the 0·55-gamma peak of ^{76}As, the annihilation radiation of ^{64}Cu and ^{65}Zn and the 0·435-MeV ray of ^{69}Zn. About 70 hr after the end of the irradiation the activity of ^{64}Cu will be negligible. The 0·55-MeV gamma peak of ^{76}As can, however, cause major difficulties, because the waiting period for complete decay of this isotope would cause a long delay; the interference is negligible for ratios of antimony:arsenic larger than 20 after a waiting period of 3 days. Simultaneous determination of both elements is also feasible by gamma spectrometry, without chemical separation, and will be described in detail elsewhere. For ratios of zinc:antimony smaller than 15 the interference is still within 1% as was the case with our samples.

TABLE II —INTERFERING ACTIVITIES

Isotope	Occurrence, %	Activation cross-section, *barn*	Isotope formed	Half life	Gamma energy, *Mev*
^{75}As	100	4 3	^{76}As	26 5 hr	0 55; 0·64; 1·20 1·78, 2 10; 2 80
^{63}Cu	69 1	3 0	^{64}Cu	12 8 hr	0 511; 1 34
^{65}Cu	30 9	0 65	^{66}Cu	5 1 min	0 83; 1 04
^{64}Zn	48 9	0 25	^{65}Zn	245 day	0 511; 1 11
^{68}Zn	18 56	0 02	^{69m}Zn	13 8 hr	0 438
^{70}Zn	0 62	4 8	^{71m}Zn	3 hr	0 38, 0 49, 0 61
^{107}Ag	51 53	23	^{108}Ag	2 3 min	0 430; 0 511; 0 600, 0 630
^{109}Ag	48 65	54	^{110}Ag	24 2 sec	0 660; 0 720 0 810; 0 880 0 940
		1 4	^{110m}Ag	270 day	0 656; 0 681, 0 706, 0 764; 0 884; 0 940, 1 381; 1 481
^{112}Sn	0 95	0 013	^{113}Sn	112 day	0 260, 0 392
^{116}Sn	14 24	0 001	^{117m}Sn	14 day	0 161; 0 320
^{122}Sn	4 71	0 007	^{123}Sn	40 min	0 153
^{124}Sn	5 98	0 01	^{125m}Sn	9 5 min	0 326
^{23}Na	100	0 54	^{24}Na	14 8 hr	1 38, 2 76

Self-shielding effects

Plumb and Lewis[6] have investigated the specific activity of ^{122}Sb and ^{124}Sb as a function of sample size and concluded that self-shielding effects were very large for the former isotope even with very small samples. This is because of the fact that ^{121}Sb has a very large resonance peak of 1,300 barn at a neutron energy of 6 eV. This effect was confirmed by irradiating an antimony sphere of 0·7 cm in the reactor core of BR-1 at a flux of 8×10^{11} neutrons/cm^2/sec. After irradiation this sphere was dissolved stepwise in hydrochloric acid–nitric acid mixtures. By weighing the antimony sphere after each step it thus became possible to determine the specific activity as a function of the radius. From Fig. 2 (curve 1) it appears that the activity of ^{122}Sb decreases exponentially in the outer 500 μ of the sphere and tends towards a constant value afterwards. ^{124}Sb shows a similar behaviour (Fig. 2, curve 2).

From this experiment it is apparent that self-shielding in an antimony standard can only be avoided by shielding with at least 0·5-mm antimony foil. Another alternative would be to dilute the standard with an inert material such as graphite The specific activity of ^{122}Sb as a function of concentration in high purity graphite is given in Fig. 3 (curve 1). From this it appears that antimony (as Sb_2O_3) should be diluted with at least 50 parts of graphite before a constant specific activity is obtained.

It could, of course, also be expected that a similar problem will occur in the lead samples. From Fig. 3 (curve 2) it appears that the upper concentration of antimony in lead is about 1 %.

External gold standard

Leliaert *et al.*[7,8] have shown that self-shielding problems and neutron flux irregularities can be avoided by the use of an internal standard. This technique is, however,

not applicable where self-shielding is from resonance peaks which do not appear in the internal standard. To avoid these problems preference was, therefore, given to the use of a gold standard spotted on the lead samples Gold was chosen as a standard because it offers the following advantages:

1. Gold is monoisotopic, giving rise by an (n, γ) reaction to ^{198}Au with a large activation cross-section ($\sigma = 98$ barns).

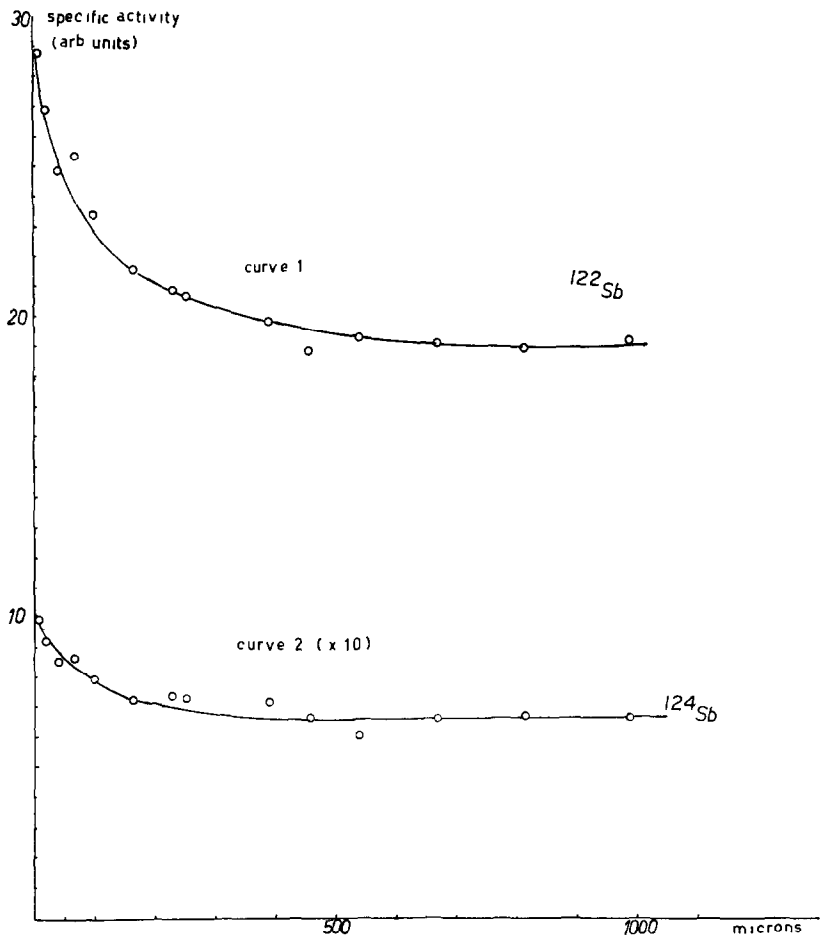


FIG 2 —Specific activity of ^{122}Sb as a function of sphere radius

2. The half life of ^{198}Au (2·69 day) is very close to the half life of ^{122}Sb (2·80 day) so that the ratio of the induced activities is practically independent of the irradiation time and of the decay period after irradiation
3. ^{198}Au emits for almost 100% a gamma of 0·40 MeV which can be easily resolved from the 0·56 MeV of ^{122}Sb with a NaI(Tl) detector of good resolution. The other gammas of 1·09 MeV (0·16%) and 0·68 MeV (0·82%) are very weak and do not interfere.

Consequently, when the lead samples are spotted with a standard solution of a gold salt, the antimony content can be computed from the following equation:

$$\% \text{ Sb} = \frac{C_{(t)}}{s} \cdot \frac{h^{122}\text{Sb}}{h^{198}\text{Au}} \tag{1}$$

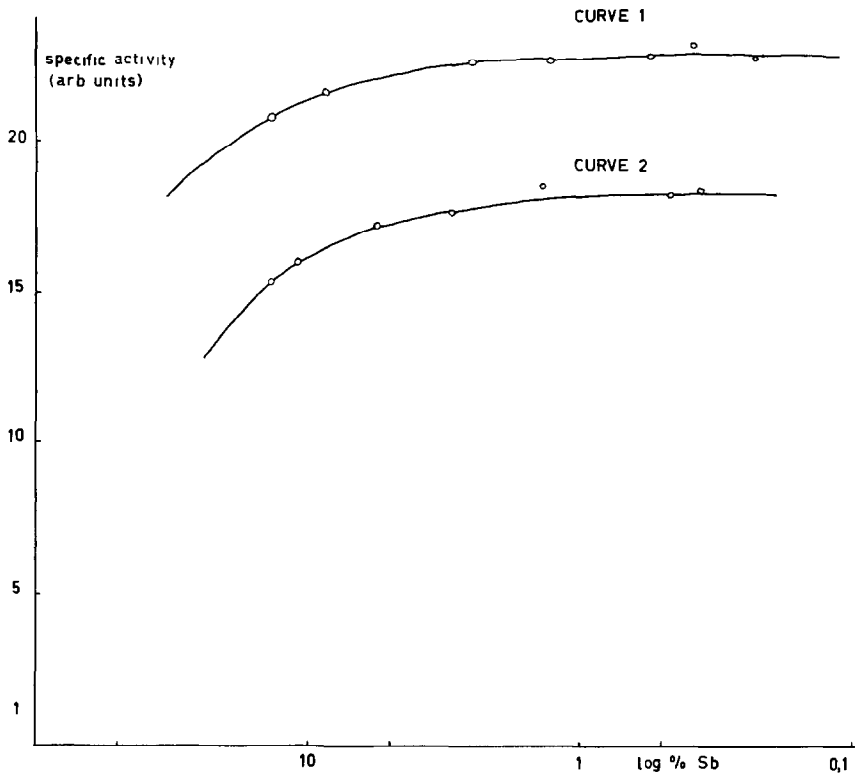


FIG 3 —Specific activity of ^{122}Sb as a function of concentration in graphite and lead.

where $C_{(t)}$ = proportionality constant,
s = sample weight,
h^{122}Sb = height of the 0·56-MeV peak of ^{122}Sb,
and h^{198}Au = height of the 0·40-MeV peak of ^{198}Au.

The constant $C_{(t)}$ is dependent upon the amount of gold used and the decay period after the end of the irradiation:

$$C_{(t)} = C_0 \exp\left(-0{\cdot}693\left(\frac{1}{2{\cdot}80} - \frac{1}{2{\cdot}69}\right)\right) \tag{2}$$

^{124}Sb is, however, simultaneously produced with ^{122}Sb. The former emits a gamma of 0·60 MeV which interferes with the height measurement of the 0·56-MeV gamma of the latter. Assuming a 5 min irradiation and taking into account the respective cross-sections, half lifes and decay modes, it is possible to compute the percentage interference of this isotope. From the activation cross-sections of ^{121}Sb and ^{124}Sb and the respective half lives, the ratio of the activities appears to be *ca* 74 for an irradiation

period of 1 min. Taking into account that the 0·56-MeV ray of ^{122}Sb occurs in 66% of the decay mode, whereas the 0·60 MeV gamma of ^{124}Sb occurs for 99%, the respective peak to total ratios and the resolution as a function of energy as given by De Soete and Hoste,[9] it can be computed that the interference of the 0·60-MeV line in the measurement of the height of the 0·56 MeV will be, respectively, 0·61, 0·78 and 1·00% after, respectively, a 0-hr, 24-hr and 48-hr waiting period. These are in good agreement with the experimental values of 0·6, 0·75 and 0·95.

Furthermore, it is obvious that the amount of gold should be chosen so as to

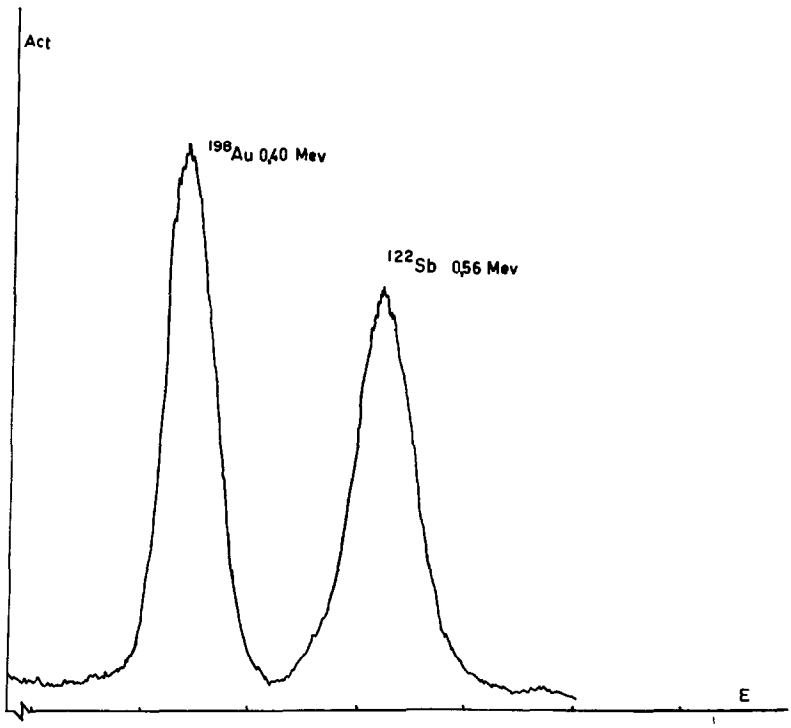


FIG 4 —Compton compensated spectrum of ^{122}Sb and ^{198}Au.

obtain a peak height of the same order of magnitude as the 0·560-MeV peak of ^{122}Sb. Moreover, equation (1) is valid for net photopeaks only. This can be achieved by the method described by Peirson *et al.*[10,11,12] According to these authors net photopeaks are obtained by subtracting the Compton continuum of the NaI(Tl) detector with a second detector equiped with an anthracene crystal, after correct equilisation for pulse height and count rate. Because equalisation of count rate with the variable switching unit recommended by Peirson appeared to be quite delicate and introduces a large dead time, a complete single channel analyser was used for each detector, the signals being fed to a differential rate meter. Correct count rate equalisation was achieved by adjusting the symmetry arrangement of the two detectors. A typical compensated spectrum of ^{198}Au + ^{122}Sb is given in Fig. 4.

In all of the experiments the count rate was determined from the peak height because this procedure gives rise to a smaller error than measurement of the photopeak area. A series of net gamma spectra were recorded for ^{198}Au and ^{122}Sb with

increasing count rates. It appeared that up to 5×10^5 cpm the standard deviation was *ca.* 2·5%.

Reliable results are, however, only possible with highly stable instrumentation: multiplier phototube with stable gain as a function of count rate, high quality high voltage, stabilised linear amplifier and pulse height analyser and a thermostatically controlled counting room within 0·5°. In these conditions the shift over a period of several weeks is completely negligible.

EXPERIMENTAL

Apparatus

Nuclear Enterprises linear amplifier 5202 and associated pulse height analyser 5102.
Tracerlab precision high voltage supply RLI-7 (common for both detector operating at *ca.* 950 V).
Hilger and Watts NaI(Tl) detector with EMI 9531 A photomultiplier (integral assembly); resolution for the 0 663 line: 8·9%.
Differential count-rate meter
Philips XY recorder, type PR 2220 A.

Procedure

The lead samples (weight *ca.* 0 5 g, diam. 1 cm) are spotted with 100 μl of a standardised gold chloride solution (5 mg of gold/ml). The solvent is evaporated under an infrared heater in the

TABLE III.—ACTIVATION ANALYSIS OF LEAD ALLOYS

Sb taken, %	Sample weight, *g*	Sb found, %	Average
0 926	0 3249	0 928	0 927
	0 3906	0 942	
LB 2	0 3750	0 920	s = 1%
	0 3566	0 919	
	0 3611	0 929	
0 854	0 3465	0 842	0 844
	0 3512	0 821	
LB 3	0 3870	0 849	s = 1·6%
	0 3741	0 859	
	0 3218	0 858	
0 231	0 4867	0 226	0 220
	0 4412	0 236	
	0 4734	0 234	s = 2%
	0 5099	0 231	
	0 5053	0 224	
0·197	0 5233	0 190	0 196
	0 5101	0 201	
	0 5309	0 196	s = 2 4%
	0 4867	0 201	
	0 4912	0 192	
0 0577	0 5155	0 0545	0 0573
	0 5143	0 0595	
	0 5433	0 0562	s = 3 7%
	0 5527	0 0593	
	0 5868	0 0570	
0 0433	0 5229	0 0440	0 0443
	0 5667	0 0427	
	0 5439	0 0433	s = 6%
	0 5970	0 0491	
	0 5672	0 0425	
0 0303	0 5765	0 0321	0 0315
	0 5751	0 0310	
	0 5430	0 0344	s = 5·4%
	0 5971	0 0298	
	0 5623	0 0307	

presence of hydrazine to avoid losses of the volatile gold chloride The gold-plated sample is wrapped in aluminium foil, packed in a standard can and irradiated in the core of BR-1 at a flux of 8×10^{11} neutrons/cm²/sec for 3 min A net photopeak spectrum is recorded after a waiting period of a few hr at a scanning speed of the bias voltage of 1 V/50 sec (time constant of rate meter: 10 sec) For antimony contents of *ca* 1% a rate meter range of 25 K was chosen because this gives rise to peak heights of *ca* 60 scale divisions on the paper strip For lower antimony contents, correspondingly lower amounts of gold and longer irradiation periods of up to 1 hr were used Using this technique a complete analysis can be performed within 0 5 hr to 1 5 hr depending on the required irradiation time

The proportionality constant C_0 was determined with Johnson Matthey Standard LB 1–LB 5 for the concentration range from 1 to 0 6% whereas the lower concentrations (down to 0 03%) were made by mixing antimony powder (200 mesh) with lead powder (100 mesh) and pressing the mixtures into pellets of *ca.* 0 5 g, diam 0 5″, at a pressure of 100,000 lb/sq inch Homogeneous mixtures of lower antimony content could not be prepared with this technique The results of a number of analyses are given in Table III

From Table III it is apparent that in the concentration range of 1% to 0·1% the standard deviation is within 2·5% which compares favourably with other instrumental methods, whereas down to concentrations of 0·03% the standard deviation is still only 5–6%. An antimony content of 0·03% does not, of course, represent the lower limit of the proposed technique. An irradiation of 1 hr at 10^{12} neutron cm²/sec would yield 12,000 cpm per μg of antimony.

Acknowledgment—This work is part of the research sponsored by the Interuniversitair Instituut voor Kernwetenschappen.

Zusammenfassung—Eine nicht-destruktive Methode zur Bestimmung von Antimon in Blei im Konzentrationsgebiet von 1–0,03%, mit Hilfe eines Goldstandards, wird beschrieben Peirsongammaspektrometrie wurde angewand und der Antimongehalt aus dem Verhaltnis der 0,40 und 0,56 MeV Aktivitaten der ^{198}Au und ^{122}Sb Isotopen berechnet Die Methode kann fur kleinere Antimongehalten erweitert werden, und ist auch auf andere Aktivierungsanalytische Probleme anwendbar

Résumé—Les auteurs décrivent une méthode non-destructive pour le dosage de l'antimoine dans de plomb, par analyse par activation en utilisant un étalon d'or On peut calculer la teneur en antimoine à partir du rapport des hauteurs des pics de 0 40 MeV et 0 56 MeV de l'or et de l'antimoine On a utilisé à cet effet un spectromètre gamma à soustraction Compton selon le procédé de Peirson On a appliqué la méthode à des échantillons dont la concentration en antimoine variait de 0 03 à 1%, avec possibilité d'étendre la mesure à des teneurs en antimoine encore plus faibles

REFERENCES

[1] G Leliaert, J Hoste and Z. Eeckhaut, *Analyt Chim Acta*, 1958, **19,** 100
[2] *Idem, Talanta*, 1959, **2,** 115
[3] J Hoste, P Bouten and F. Adams, *Nucleonics*, 1961, **19,** 118
[4] P Bouten and J Hoste, *Talanta*, 1961, **8,** 322
[5] W. Bock-Werthmann and W Schulze, AED C-14-1
[6] A. C. Plumb and J E Lewis, *Nucleonics*, 1955, **13,** 45.
[7] G Leliaert, J Hoste and Z Eeckhaut, *Nature*, 1959, **182,** 600.
[8] J Hoste, *J Pure and Appl Chem*, 1960, **1,** 99
[9] D. de Soete and J Hoste, *Modern Trends in Activation Analysis*, College Station, Texas, 1961-CAA/12
[10] D H Peirson, *Nature*, 1954, **173,** 990
[11] D H. Peirson, *Brit. J. Appl Phys*, 1955, **6,** 444
[12] D H Peirson and P Iredale, UNESCO Conference, (Paris, 1957)

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AMMONIUM HEXANITRATOCERATE(IV) AS AN OXIDISING AGENT

TITRATION OF OXALIC AND MANDELIC ACIDS AT ROOM TEMPERATURE

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Summary—The use of ammonium hexanitratocerate(IV) in oxidimetry has been very little studied, although the salt can be obtained in a high degree of purity Conditions have now been established for the titration of oxalic and mandelic acids with this reagent at room temperature in a nitric or hydrochloric acid medium using ferroin as indicator The procedures developed give precise results and they constitute definite improvements over those involving cerium^{IV} sulphate

SMITH, Sullivan and Frank[1] described the preparation of ammonium hexanitratocerate(IV) in a high degree of purity and studied its stability in aqueous solution acidified with nitric or sulphuric acid. Subsequently, Smith and Fly[2] described the preparation of ammonium hexanitratocerate(IV) in a sufficient degree of purity to be used as a primary standard. They claimed several advantages for the use of this salt: (1) high equivalent weight, (2) high degree if stability in the crystalline condition,* and (3) the attainment of a high oxidation potential in perchloric acid (1·70–1·87v from 1–8*N*) or in nitric acid (1·61–1·56v from 1–8*N*) media. Smith, Sullivan and Frank[1] determined the purity of the salt by dissolving a weighed sample in sulphuric acid (1:10) and titrating with standard iron^{II} sulphate solution, using ferroin as indicator. Smith and Fly[2] determined the purity of the salt by dissolving weighed samples in 70% perchloric acid and titrating with a standard solution of sodium oxalate in perchloric acid solution, using nitroferroin as indicator. This reverse titration is preferred to the usual direct titration for reasons fully discussed in their original paper.

The use of ammonium hexanitratocerate(IV) in a nitric acid medium does not appear to have been studied although Smith, Sullivan and Frank stated that "The nitrate ion had no influence upon the determination of ferrous iron, the most commonly determined element. It is not expected to interfere in most cases. The value of the proposed new standard need not be in the least minimised by such considerations From a solution of known weight of ammonium hexanitratocerate in sulphuric acid, a solution of ceric ammonium sulphate is easily obtained free from nitric acid by the simple process of digestion. All question of the possible presence of the undesirable nitrate ion is thus eliminated."

The process of digestion with sulphuric acid to eliminate the nitrate ion is to be

* The reagent is somewhat unstable in solution and requires frequent standardisation.

avoided for three reasons: (1) it is tedious, (2) it deprives the advantage of this complex salt as a primary standard, and (3) the conversion of the ammonium hexanitratocerate(IV) to cerium^{IV} ammonium sulphate as proposed by Smith, Sullivan and Frank[1] will remove its advantages as a reagent of high oxidation potential. Further, according to Smith and Fly,[2] the preparation of a solution of ammonium hexanitratocerate(IV) in a sulphuric acid medium requires great care, otherwise mixed insoluble nitratosulphatocerates may be precipitated. Although a higher oxidation potential of the ammonium hexanitratocerate(IV) can be utilised by working with solutions of the salt in a perchloric acid medium, there are some difficulties associated with this reagent as discussed fully by Smith and Fly.[2]

A survey of the literature has shown that so far no one has extensively studied the reagent in a nitric acid medium, using ferroin as indicator. We have now made a study of this reagent both in nitric acid and hydrochloric acid media. Our results are somewhat at variance with the statement of Smith, Sullivan and Frank about the non-interference of nitric acid. We have ascertained the concentrations of nitric acid under which iron^{II} and oxalate can be titrated accurately with the cerate solution at room temperature.

EXPERIMENTAL

Reagents

Ammonium hexanitratocerate(IV) solution The crystalline complex salt is prepared according to the method of Smith *et al*[1] A known weight of the solid thus obtained is dissolved in nitric acid and the solution made up to 1 litre with the requisite amount of dilute nitric acid so that the overall concentration of nitric acid is 1 0*N* Although Smith *et al* experienced some difficulty in the preparation of clear solutions of ammonium hexanitratocerate(IV) in 1 0*N* perchloric acid because of the precipitation of complex perchloratonitratocerates, no such difficulty has been experienced by us in the preparation of a nitric acid solution of this reagent The solution is stored in an amber coloured Jena glass bottle The solution is standardised against a solution of Mohr's salt in a sulphuric acid medium, using ferroin as indicator, the Mohr's salt solution having been previously standardised against a standard cerium^{IV} sulphate solution which in its turn has been standardised against a standard solution of reagent grade sodium oxalate with a potentiometric end-point

All other reagents employed in this investigation were of analytical reagent grade

Titration of iron^{II}

Titration in a sulphuric acid medium From 5 0–10 0 ml of an approx 0 05*N* iron^{II} solution (prepared by dissolving iron wire of AnalaR grade in sulphuric acid and adjusting the overall sulphuric acid concentration to about 1*N*) were taken in an Erlenmeyer flask and treated with 20 ml of 2*N* sulphuric acid and 20 ml of distilled water The mixture was treated with 0 5 ml of 0 001*M* ferroin then titrated with the ammonium hexanitratocerate(IV) solution with constant stirring until a permanent pale blue colour persisted

The indicator correction is negligible in titrations with 0 1–0 05*N* solutions of the cerate, but in titrations with 0 02–0 01*N* solutions a correction is necessary depending on the quantity of ferroin, added. Accordingly, it is convenient to dilute 0 01*M* ferroin solution 10 times and use 0 5 ml of this solution each time as indicator The indicator correction can then be precisely applied.

Titration in a nitric acid medium. Iron^{II} can be titrated in 1 0*N* nitric acid using ferroin as indicator, provided the iron^{II} solution is not kept for more than 5–10 min after the addition of nitric acid If the mixture is allowed to stand longer, the iron^{II} is oxidised slowly by the nitric acid, leading to low titres and sluggish end-points. This difficulty is enhanced by increasing the concentration of nitric acid. A closer study of the matter revealed that difficulty concerning the indicator action is traceable to the nitrous acid formed as a result of the reaction between iron^{II} and nitric acid Nitrous acid is capable of slowly reducing ferriin to ferroin, this reduction occurring only when all of the iron^{II} is oxidised It is, therefore, desirable to add nitric acid last to an iron^{II} solution, *i e* after the addition of water and the indicator solution In no case should nitric acid of concentration greater than 2 0*N* be added to the iron^{II} solution Using these precautions it is possible to carry out accurately the titration of even a 0 01*N* solution of iron^{II} with 0 01*N* ammonium hexanitratocerate(IV)

The reverse titration of ammonium hexanitratocerate(IV) in nitric acid with iron^{II} sulphate solution can also be carried out without difficulty using ferroin as indicator Evidently ferriin is

quite stable in contact with an excess of ammonium hexanitratocerate(IV) solution in 1·0*N* nitric acid acid without losing its reversibility as an indicator

Determination of oxalate

Kirk and Tompkins[3] carried out the microtitration of oxalate with ammonium hexanitratocerate-(IV) both in nitric acid and in perchloric acid media These authors stated that the results obtained in a nitric acid medium "are somewhat misleading in that the reaction is too slow for convenience and the end-point was difficult to read with ortho-phenanthroline ferrous sulphate particularly in presence of asbestos" Consequently, the authors did not recommend this procedure but preferred the back-titration using cerium^{IV} sulphate

We have found that the microtitration of oxalate is fairly satisfactory if the initial concentration of nitric acid in the titration mixture is 0 1–0 2*N* and if the titrant is added slowly If the concentration of nitric acid in the titration mixture exceeds 0 2*N* the end-point becomes difficult to recognise, the difficulty increasing with increasing concentration of the acid Our experiments show that this difficulty in detecting the end-point arises from two factors· (1) the reduction of the light blue ferriin by oxalate to the red ferroin is slow; (2) as the titration progresses there is a gradual decrease in the intensity of the ferroin red colour, with the result that the red colour reaches only a small fraction of its original intensity near the end-point even after waiting for some time Curiously enough this difficulty is enhanced when the speed of addition of the cerium^{IV} salt is increased For these reasons the transition from the very light red colour to the very light blue colour is difficult to notice in macrotitrations.

Significant observations made during attempted macrotitrations of oxalate with ammonium hexanitratocerate(IV) in a nitric acid medium are summarised as follows

(1) During the early stages of the titration, on the addition of each portion of the cerate solution the ferroin red colour changes to the yellow colour of the cerium^{IV} which gradually changes to red, through orange, in about 6–8 sec, the intensity of the restored red colour is somewhat less than that at the start of the titration

(2) The intensity of the restored red colour, as stated above, becomes less and less as the equivalence point is approached

(3) The loss in intensity of the ferroin red colour increases as the nitric acid concentration of the titration mixture is increased, so that in titrations carried out in media of nitric acid concentrations greater than 0 2*N* the colour transition at the equivalence point is difficult to discern

(4) Macrotitrations of oxalate are not possible, even in 0 1–0 2*N* nitric acid media, because of the difficulties pointed out above

We have made the interesting observation that the addition of a little potassium iodide or iodate (1 ml of $10^{-3}M$ solution per 50 ml of titration mixture) eliminates these difficulties; both the micro and macrotitrations can then be accurately carried out in nitric acid media ranging from 0 1 to 0 8*N* When potassium iodide is used in the mentioned amount, an extra consumption of cerate (0 1 ml of 0 01*N* solution) is required and a correspondingly lesser amount of cerate when potassium iodate is used It has also been noticed that the correction is negligible when a mixture of potassium iodide and iodate to give a concentration of iodine equivalent to that of potassium iodide used above is employed When titrations are made using any of these catalysts, the ferroin red colour remains almost the same in intensity throughout the course of the titration Hence the transition from red to light blue can be sharply perceived at the equivalence point, both in micro and macro titrations when the nitric acid concentration lies between 0 1 and 0 8*N* However, when the acid concentration is raised to 1 0*N* or above, the fading of the ferroin colour again makes itself felt, and the titrations become difficult even in the presence of the above mentioned catalysts In our opinion the action of the catalyst is more concerned with the functioning of the indicator rather than with the reaction of cerate with oxalate Further work is in progress to elucidate the mechanism of the action of the catalyst

Recommended procedure for the titration of oxalate in a nitric acid medium Take 5–10 ml of the oxalate solution in a 100-ml Erlenmeyer flask and treat with 40 ml of 0 5–0 8*N* nitric acid, 0 5 ml of 0 001*M* ferroin and 1 ml of a mixture of potassium iodide and potassium iodate (equivalent to $10^{-3}N$ iodine) Titrate with a solution of ammonium hexanitratocerate(IV) till the ferroin red colour just changes to very pale blue If the blue colour reverts to a pale red tinge in 10–15 sec, a fraction of a drop of the cerate solution may be added to obtain a permanent pale blue colour

A large number of micro and macro titrations have been made according to this procedure Some typical results are given in Table I

Titration of oxalate in a hydrochloric acid medium. Oxalate can be conveniently titrated in 0 2–0 5*N* hydrochloric acid at room temperature with ammonium hexanitratocerate(IV) using ferroin as indicator. The fading of the ferroin colour noticed during titrations in a nitric acid medium is not so much in evidence here Accurate results have been obtained both in titrations with 0 05*N* and 0 01*N*

TABLE I —DETERMINATION OF OXALATE BY AMMONIUM HEXANITRATOCERATE(IV) IN A NITRIC ACID MEDIUM

Oxalate taken, *mmoles*	Oxalate found, *mmoles*	Oxalate taken, *mmoles*	Oxalate found, *mmoles*
2 3000	2 2900	0 1600	0 1601
1 2000	1 2010	0 1200	0 1202
0 5600	0 5610	0 0860	0 0859
0 4500	0 4508	0 0590	0 0588
0 3400	0 3401	0 0350	0 0351
0 2300	0 2295	0 0240	0 0241

cerate solutions When the concentration of hydrochloric acid is raised to 1 0*N* or above, an increasing fading of the ferroin colour is noticed, and the titration becomes almost impossible in a 2·0*N* hydrochloric acid medium The use of iodide-iodate mixture, however, enables the titration to be made with the usual facility, even in 2 0*N* hydrochloric acid

The titration[5] of oxalic acid with cerium^{IV} sulphate at room temperature in the presence of barium ion as a scavenger for sulphate ion is subject to the limitation that the colour of the ferroin indicator is somewhat masked by the precipitated barium sulphate The present method, involving the use of ammonium hexanitratocerate(IV) in a nitric acid or hydrochloric acid medium, does not suffer from this disadvantage.

Determnation of mandelic acid

Titration of mandelic acid is not possible in either nitric acid or hydrochloric acid media, even of very low concentration, without the use of the catalyst This is because the ferroin red colour does not return about 0 2–0 3 ml before the equivalence point, even after waiting for 10–15 min

If the catalyst is added at the stage when the ferroin colour fades very much (about 0 4–0 5 ml before the equivalence point), however, the red colour is regained in good intensity and the titration can be carried out without any further difficulty In view of these findings, the following procedure is recommended for the titrimetric determination of mandelic acid

Take 5–10 ml of mandelic acid solution (0 01–0 05*N*) in an Erlenmeyer flask, then add 40–45 ml of 0 2*N* nitric acid (or hydrochloric acid) and 0 5 ml of 0 001*M* ferroin Titrate with a solution of ammonium hexanitratocerate(IV) of appropriate strength Near the equivalence point when the ferroin red colour has faded very much, add 0 5 ml of potassium iodide-iodate mixture (equivalent to 10^{-3}*N* iodine) and continue the titration dropwise until a permanent light blue colour is obtained

A large number of titrations have been carried out as described above Some typical results are given in the Table II

TABLE II —TITRIMETRIC DETERMINATION OF MANDELIC ACID WITH AMMONIUM HEXANITRATOCERATE(IV)

Mandelic acid, *mmoles*	
Taken	Found
0 6800	0 6805
0 6000	0 5980
0 5500	0 5507
0 5300	0 5285
0 4300	0 4310
0 2300	0 2290
0 1300	0 1290
0 0965	0 0966
0 0595	0 0595

The direct titrimetric procedure now developed for the determination of mandelic acid is an improvement over the procedure of Verma and Paul,[4] which consists of adding an excess of cerium^{IV} sulphate to an aliquot of the mandelic acid solution, allowing to react for 5 min, then titrating the excess cerium^{IV} with standard iron^{II} sulphate solution

Zusammenfassung—Obwohl das Salz in hohem Reinheitsgrad erhaltlich ist wurde die Anwendung von Ammonium hexanitrato cerate in der Oxydimetrie nur wenig studiert. Bedingungen wurden ausgearbeitet um Oxalsaure und Mandelsaure mit dem Reagens bei Zimmertemperatur in salpeter- oder salsaurem Medium zu titrieren. Ferroin wird als Indicator verwendet. Die neu entwickelte Methode gibt genaue Resultate Die Methode hat Vorteile gegenuber der Verwendung von Cersulfat.

Résumé—L'utilisation d'hexanitratocérate d'ammonium en oxydimétrie a été très peu étudiée, bien que le sel puisse être obtenu avec une très grande pureté. Les conditions de titrage par ce réactif des acides oxalique et mandélique ont été établies à la température ambiante en milieu acide nitrique ou chlorhydrique en utilisant la ferroïne comme indicateur interne. Les méthodes ainsi mises au point donnent des résultats précis. Elles constituent de nettes améliorations sur les méthodes mettant en jeu le sulfate de cérium(IV) comme réactif

REFERENCES

[1] G F. Smith, V. R. Sullivan and G. Frank, *Ind Eng. Chem , Analyt* , 1936, **8,** 449.
[2] G. F. Smith and W. H Fly, *Analyt. Chem* , 1949, **21,** 1233.
[3] P L. Kirk and P. C. Tompkins, *Ind. Eng. Chem , Analyt.*, 1941, **13,** 277.
[4] M R. Verma and S. D. Paul, *J. Sci. Ind. Res., India,* 1953, **12B,** 178; 1954, **13B,** 346.
[5] V P. Rao and G G Rao, *Talanta,* 1959, **2,** 370

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IDENTIFICATION OF POLYATOMIC ANIONS BY INFRARED SPECTROSCOPY

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Summary—Mixtures of ferrocyanide, ferricyanide and cobalticyanide, and of chromate, vanadate and sulphate, may be identified by the characteristic infrared spectra of the anions. The relation between the intensity of the band and the concentration of anion enables quantitative measurements to be made on microgram amounts.

THE possibility of using the characteristic infrared absorption frequencies of inorganic salts for the identification of anions present in mixtures has been investigated. The anions selected for study have previously been separated by the authors,[1] using standard microanalytical techniques; each of the anions studied possesses a characteristic infrared spectrum.

Potassium ferrocyanide, ferricyanide and cobalticyanide have been studied by several workers,[2–6] who showed that these species absorbed in the region between 2100 cm^{-1} amd 2000 cm^{-1}. Generally the range 2200 cm^{-1} to 2000 cm^{-1} could be regarded as covering all the forms in which the —CN grouping occurs in inorganic compounds. The infrared spectra of the cyanide complexes of silver, copper and gold have also been studied in aqueous solution.[7–9]

Potassium ferrocyanide and ferricyanide, as shown by Emschwiller,[6] are characterised by bands which correspond to the fundamental vibration of the —CN grouping. The absorption band is much more intense for the ferrocyanide ion than for the ferricyanide ion. Experimentally, it was proved that the cobalticyanide ion spectrum resembles the ferricyanide ion spectrum.

The infrared absorption spectra of the anions chromate, vanadate and sulphate, which are assignable to the metal-oxygen[12] and sulphur-oxygen stretching frequencies, have also been examined and the results of these studies and the application of the spectra to qualitative and quantitative microanalysis are discussed in this paper. Unfortunately the alkali halide salts are transparent to infrared radiation, and hence this technique cannot be used to identify mixtures of halides, the third group of anions previously studied.[1]

The characteristic frequencies of the various anionic groups can vary within limits of about 100–200 cm^{-1}, depending on the nature of the cation and the type of bonding involved. This is particularly important in the case of complex formation, where the characteristic frequency of the anion may shift drastically from that shown by the sodium or potassium salt. Changing the cation associated with the complex anion may produce a different crystalline arrangement, resulting in a different symmetry or intensity of the electric field around a negative ion. A difference in the type or extent of hydration probably alters some of the frequencies.[2] Therefore, it is advisable to use the potassium salts of the anions as a standard basis for the study of the spectra. In

practice the interference from the cation may be eliminated by using ion exchange, to permit the detection by spectroscopy of the anion as the potassium salt.

EXPERIMENTAL

Studies on single anions

Crystals of salts containing the various anions were intimately ground with potassium bromide and pressed into a disc about 1 mm in thickness. The potassium bromide discs were prepared with a Perkin-Elmer die using an "Apex" hydraulic press with a 10-ton capacity on a ram of 2⅛-inch diameter The infrared absorption spectrum of the disc was then recorded, using a Perkin-Elmer infrared spectrophotometer (Infracord, Model 137).

Most of the anions involved in the study gave clear and transparent discs with KBr. An exception was the vanadate, which showed some opacity. But with discs with low concentration of the anion, this behaviour was negligible. The spectra of pure salts and mixtures of salts were examined and the possibility of using the infrared spectra for simultaneous qualitative and quantitative analysis was investigated.

The characteristic absorption bands of the various anions are summarised in Table I

TABLE I —CHARACTERISTIC ABSORPTION BANDS OF ANIONS

Salt	Wave no , cm^{-1}	Wavelength, μ	Relative intensity*	Reference	Notes
Potassium ferrocyanide, AnalaR, $K_4Fe(CN)_6\ 3H_2O$	1630	6·13	s sp.	2	*a*
	1650	6 07	m.	2	*a*
	2015	4 96	v s.	2	*a*
	2040	4 90	v s.	6	*a*
Potassium ferricyanide, AnalaR, $K_3Fe(CN)_6$	2100	4 77	s	2	*b*
	2115	4 73	s.	6	*b*
Potassium cobalticyanide, B.D.H , $K_3Co(CN)_6$	2100	4 77	s		*c*
	2115	4 73	s.		*c*
Potassium sulphate, AnalaR, K_2SO_4	1110	9·00	v s.	2	*d*
Potassium chromate, AnalaR, K_2CrO_4	872	11·45	v s	2	*e*
Sodium metavanadate, Hopkin and Williams, $NaVO_3 . 4H_2O$	828	12 08	s.	2	*f*
	910	11 00	v w	2	*f*
	935	10 70	s.	2	*f*
	957	10 45	s	2	*f*

* s = strong sp = sharp m = medium v. = very w = weak b = broad

Notes

(*a*) The frequencies in cm^{-1} for maximum absorption for most of the ferrocyanide salts range between 2010 for thallium ferrocyanide to 2120 for aluminium ferrocyanide.[6]

(*b*) The frequencies in cm^{-1} for maximum absorption for most of the ferricyanide salts range between 2115 for potassium ferricyanide to 2176 for copper ferricyanide. AnalaR potassium ferricyanide showed two additional bands; the first one at 1630 cm^{-1} (6·13 μ) s.sp.,[2] and the second one at 2015 cm^{-1} (4 96μ) v s.[2].

If the surface of a crystal of potassium ferricyanide (which normally shows the 2040 band) is washed and dried, only one very strong band at 2100 (2115) cm^{-1} (4 77 μ) is obtained This test indicates that AnalaR potassium ferricyanide actually contains ferrocyanide as an impurity The evidence has been confirmed by examining a synthetic mixture (1 · 1) of ferrocyanide and ferricyanide, after mixing them with KBr, on the spectrophotometer where the same bands as those given by the AnalaR ferricyanide were given.

From the figures shown in Table I, it can be observed that the bands of ferricyanide and cobalticyanide (in the potassium salts) are superimposed on each other Each of the above salts was, therefore, subjected individually to treatment with a concentrated neutral solution of KI. After drying the mixture of the two ions, it was found that ferricyanide was reduced completely to ferrocyanide and that the spectrum of ferrocyanide ion was the only one given. On the other hand cobalticyanide

was not affected It can be concluded, therefore, that potassium iodide can be used as a selective reductant for the ferricyanide.

(*c*) The frequencies in cm^{-1} for maximum absorption for most of the sulphate salts range between 1080 for zirconium sulphate to 1135 for manganese sulphate.[2] Potassium sulphate shows only one very strong band at 1110 cm^{-1} (9·0 μ).

(*d*) The frequencies in cm^{-1} for maximum absorption for most of the chromate salts (except for aluminium chromate) range between 795 for zinc chromate to 890 for sodium chromate [2] Potassium chromate gives the following distinct bands. 858 cm^{-1} (11·65 μ) w.sp. 872 cm^{-1} (11 45 μ)v s 935 cm^{-1} (10·7 μ)s

(*e*) The frequencies in cm^{-1} for maximum absorption for the two metavanadates studied[2] range from 828 for sodium metavanadate to 935 for ammonium metavanadate. Sodium metavanadate shows the characteristic bands[2] listed in Table II

TABLE II —ABSORPTION OF SODIUM METAVANADATE

Wave no , cm^{-1}	Wavelength, μ	Relative intensity
693	14 4	s b
828	12 08	s
910	11 0	v w.
935	10 7	s
957	10 45	s
3450	2·9	w b

Studies on mixtures of anions

1. *Ferrocyanide, ferricyanide and cobalticyanide* A synthetic mixture containing equal amounts of the three complex cyanides was prepared A weighed portion was mixed with KBr, and the absorption spectrum of the KBr disc was recorded. Two very strong bands appeared in the 2040 cm^{-1} and 2115 cm^{-1} regions, indicating the presence of either two or three anions in the unknown.

Another portion, of equal weight to the first, was dissolved in the minimum amount of water and a concentrated solution of KI was added. The solution was evaporated to dryness and baked in an oven at 105°. The residue obtained was mixed with KBr and again the infrared spectrum was recorded. A shift of the strong band from 2115 cm^{-1} to 2040 cm^{-1} *and* the enhancement of the 2040 cm^{-1} band indicates the presence of ferricyanide No shift proves the presence of cobalticyanide. No shift of the band 2115 cm^{-1} *and* no enhancement of the band 2040 cm^{-1} indicates the absence of ferricyanide

2. *Sulphate, chromate and metavanadate*· The infrared spectrum of a synthetic mixture of these three anions showed no interference arising from overlapping of the spectra of the corresponding individual anions, although the bands were appreciably broader than the complex cyanide bands.

3. *Six anions* Fig. 1 shows the infrared spectrum of a KBr disc containing ferrocyanide, ferricyanide, cobalticyanide, sulphate, chromate and vanadate anions. The following points may be noted:

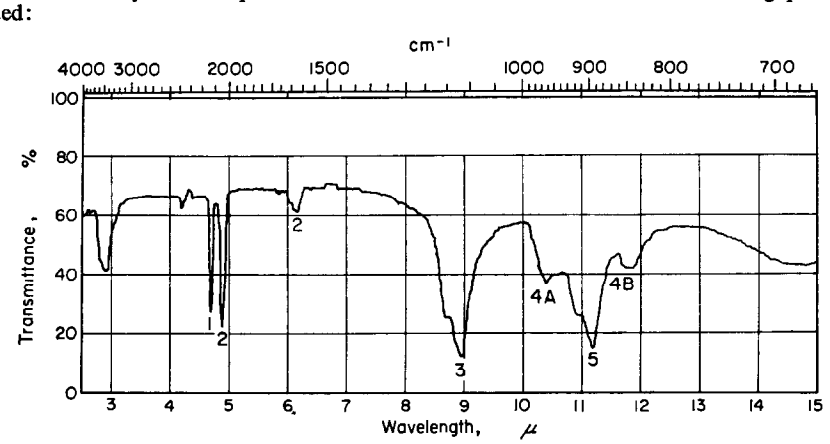


FIG 1.—Infrared spectrum of mixture of anions.

1—ferricyanide and cobalticyanide.
2—ferrocyanide.
3—Sulphate.
4—vanadate.
5—chromate.

(*a*) the bands of ferricyanide and cobalticyanide are superimposed on each other in the region 2115 cm^{-1}. For resolution of these two spectral bands, treatment with concentrated KI solution is required;
(*b*) ferrocyanide gives its characteristic band at 2040 cm^{-1},
(*c*) sulphate appears at 1110 cm^{-1};
(*d*) chromate appears at 872 cm^{-1};
(*e*) metavanadate gives two bands, one at 957 cm^{-1} and one at 828 cm^{-1}

It was possible to identify the anions from their corresponding bands if they were present in the amounts shown in Table III

TABLE III—LIMIT OF IDENTIFICATION OF ANIONS

Anion	μg
Ferrocyanide	5
Ferricyanide	20
Cobalticyanide	20
Sulphate	20
Chromate	20
Metavanadate	80

Quantitative studies

Preparation of the disc A portion of the salt containing 2 mg of the anion was weighed accurately on to the near edge of a watch glass. The salt was quantitatively transferred to an agate mortar containing 1000 mg of Specpure KBr The mixture was ground for 5 min to produce a fine, thoroughly-mixed powder Each mg of the resulting powder therefore contained 2 μg of the anion. For other experiments x mg of the powder were mixed with 200 mg of KBr, accurately weighed, and the mixture was again ground to a fine powder A disc was made from this combined powder and the spectrum was recorded on the Infracord. The intensity of the absorption at the characteristic bands was found to vary more or less linearly with the concentration of anion present. Using the Infracord, measurable intensities were obtained with microgram amounts of anion present.

DISCUSSION

It was found easier to identify microgram amounts of the selected anions by infrared spectroscopy than by the techniques described by Benedetti-Pichler[10] and other workers.[11] The infrared method is simpler and faster than the ultramicro technique. The time required to make an infrared experiment is not more than 20 minutes, while with the other technique it can take an hour or more. With the anion systems examined there was no interference between spectral bands of the individual anions, and each of the anions had a characteristic absorption band. The number of anionic species which possess such characteristic infrared absorption peaks, is, however, limited. For example, the alkali halide salts are transparent to these radiations and hence this technique cannot be used to identify mixtures of halides. On the other hand, there are other polyatomic anion species which should absorb infrared radiation. These are being examined, and work is also proceeding to extend the applications of this technique to microanalysis.

Because there is a linear relationship between intensity of absorption and amount of anion present, it should be possible to develop further sensitive qualitative and quantitative separation procedures.

Zusammenfassung—Eine infrarotspektrophotometrische Methode wurde entwickelt um die folgenden Anionen in Mikrogrammengen von Mischungen zu nachweisen und zu bestimmen· Ferrocyanid, Ferricyanid, Kobalticyanid; und Chromat, Vanadate, Sulfat

Résumé—Les auteurs ont mis au point une methode de spectroscopie d'absorption infra-rouge permettant l'identification et le dosage de microgrammes des melanges des anions suivant: ferrocyanure, ferricyanure, cobalticyanure; et chromate, vanadate, sulfate.

REFERENCES

[1] F R. Haba and C L Wilson, *Proceedings of the Feigl Anniversary Symposium*, Birmingham, 1962, in press.
[2] F. A. Miller and C H. Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.
[3] G B. Bonino and G. Fabbri, *Atti. Accad. naz Lincei, Rend Classe Sci fis mat nat*, 1956, **21**, 246.
[4] *Idem, ibid*, 1955, **19**, 386; 1956, **20**, 414.
[5] G. B. Bonino and O Salvetti, *ibid*, 1956, **20**, 150.
[6] Guy Emschwiller, *Compt. rend.*, 1954, **238**, 1414
[7] L. H. Jones and R A. Pennemann, *J. Chem Phys.*, 1954, **22**, 965.
[8] L. H. Jones, *ibid.*, 1954, **22**, 1135.
[9] R. H. Pennemann and L. H Jones, *ibid.*, 1956, **24**, 293.
[10] A. A. Benedetti-Pichler, *Introduction to the Microtechnique of Inorganic Analysis*. John Wiley and Sons, Inc., New York, 1959
[11] H. M. El-Badry and C. L. Wilson, *Mikrochim. Acta*, 1952, **40**, 141.
[12] C G Barraclaugh, J. Lewis and R S. Nyholm, *J. Chem Soc*, 1959, 3552.

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QUANTITATIVE TREATMENT OF EXCHANGE EQUILIBRIA INVOLVING COMPLEXANS—I

POLAROGRAPHIC DETERMINATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM

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Summary—In order to find optimum conditions for the indirect polarographic determination of calcium, a quantitative consideration is made of the following exchange equilibrium:

$$MY + Ca + nNH_3 \rightleftharpoons M(NH_3)_n + CaY.$$

The use of Cd-EGTA is proposed for the selective determination of calcium in the presence of a large excess of magnesium

DIFFICULTIES are encountered in the polarographic determination of such elements as calcium and magnesium which do not give a well-defined reduction wave at the dropping mercury electrode in a suitable potential range. However, the indirect polarographic determination of such elements is sometimes successful by utilising an appropriate exchange reaction. Thus, Přibil *et al.*[1,2] proposed a novel method in which an ammoniacal Zn-EDTA solution was added to the sample solution and the zinc-ammine complex liberated by calcium was determined polarographically. Sensitive though the method is, the sum of calcium and magnesium is determined when the two are present together. Přibil *et al.* claimed to be able to determine calcium in the presence of five times as much as magnesium, precipitating the latter as magnesium ammonium phosphate. In the present work attention was drawn to the difference in stability constants between the EGTA [ethyleneglycol-*bis*-(β-aminoethyl ether)-N:N′-tetra-acetic acid] chelates of calcium and magnesium, and a procedure was developed for the selective polarographic determination of calcium in mixtures containing a large excess of magnesium. Quantitative consideration of the exchange equilibrium involved[3] led to the use of Cd-EGTA instead of Zn-EGTA.

Choice of complexan

The exchange equilibrium involving MY and calcium ion in ammoniacal media may be described (omitting charges for simplicity) as follows:

$$MY + Ca + nNH_3 \rightleftharpoons M(NH_3)_n + CaY \qquad (1)$$

where M represents Cd or Zn (see the following section). If M is added as MY

($[M]_t = [Y]_t$) and NH_3 designated as A, from an equation (10) derived elsewhere[3]

$$[Ca]_t = \left([MA_4] - \frac{[M]_t - [MA_4]}{[MA_4]} \cdot K_2[A]^4\right)\left(1 + \frac{[MA_4]}{[M]_t - [MA_4]} \cdot \frac{1}{K_1[A]^4}\right) \quad (2)^*$$

where

$$K_1 = K_{CaY}K_{MA_4}/K_{MY} \text{ and } K_2 = K_{MA_4}\alpha_{H(Y)}/K_{MY}.$$

In (2) the term $\frac{[M]_t - [MA_4]}{[MA_4]} \cdot K_2[A]^4$ may be neglected in comparison with $[MA_4]$ if $K_2[A]^4$ is sufficiently low. Thus

$$[Ca]_t = [MA_4]\left(1 + \frac{[MA_4]}{[M]_t - [MA_4]} \cdot \frac{1}{K_1[A]^4}\right) \quad (3)$$

The second term in the parentheses of (3) may be neglected provided $K_1[A]^4$ is sufficiently high or $\frac{[MA_4]}{[M]_t - [MA_4]}$ is sufficiently low, and then:

$$[Ca]_t = [MA_4] \quad (4)$$

In order to apply (4) to a wider range of calcium concentration, $K_1[A]^4$ should be sufficiently high and $K_2[A]^4$ sufficiently low. In the range where (4) holds calcium can be successfully determined by means of polarography of MA_4.† It must be borne in mind that, the relationship $K_1/K_2 = K'_{CaY}$ existing always, K'_{CaY} of higher than 10^6 is preferable for the successful indirect polarographic determination of calcium according to exchange equilibrium (1).‡

In Fig. 1 $[MA_4]/[M]_t$ is plotted against $[Ca]_t/[M]_t$ for various values of $K_1[A]^4$. The higher the value of $K_1[A]^4$ is, the wider is the range where (4) holds, *i.e.* $[Ca]_t$ is proportional to $[MA_4]$ to a value of $[Ca]_t/[M]_t$ more close to unity. From Fig. 1 it is also obvious that $K_1[A]^4$ should be more than 10^2 in order to apply (4) to a point $[Ca]_t/[M]_t = 0{\cdot}5$.

The same considerations for the case of magnesium yields:

$$[Mg]_t = [MA_4]\left(1 + \frac{[MA_4]}{[M]_t - [MA_4]} \cdot \frac{1}{K_1'[A]^4}\right) \quad (5)$$

where $K_1' = K_{MgY}K_{MA_4}/K_{MY}$.§ In Fig. 2 $[MA_4]/[M]_t$ is plotted against $[Mg]_t/[M]_t$ for various values of $K_1'[A]^4$. For sufficiently low values of $K_1'[A]^4$ ($<10^{-3}$), the amount of MA_4 liberated by magnesium is very small and can be neglected. In order to be successful in the selective determination of calcium in the presence of magnesium, $K_1[A]^4$ should be sufficiently high and $K_1'[A]^4$ should be sufficiently low. Because $K_1[A]^4/K_1'[A]^4 = K_{CaY}/K_{MgY}$, a complexan should be chosen for which the difference in stabilities between its calcium and magnesium chelates is large.

* In the case of zinc and cadmium, n = 4 when $[NH_3] = 0{\cdot}1 \sim 1M$.

† The limiting current of MA_4 may be practically regarded as diffusion-controlled and its wave-height is proportional to the concentration of MA_4 in the bulk of the solution

‡ In an ammoniacal solution (pH $\geqq$ 10), it is not difficult to find a complexan forming a calcium chelate of apparent stability constant higher than 10^{10}: $\log K_{Ca\text{-}EDTA} = 10{\cdot}7$, $\log K_{Ca\text{-}EGTA} = 11\,0$, *etc.* Thus in these cases it is possible to realise a sufficiently high value of $K_1[A]^4$ ($>10^8$) together with a sufficiently low value of $K_2[A]^4$ ($<10^{-3}$).

§ The ammine complexes of magnesium are not very stable and their formation may be practically neglected: $[Mg]_t/[Mg] < 3$ in $1M$ ammonia solution.

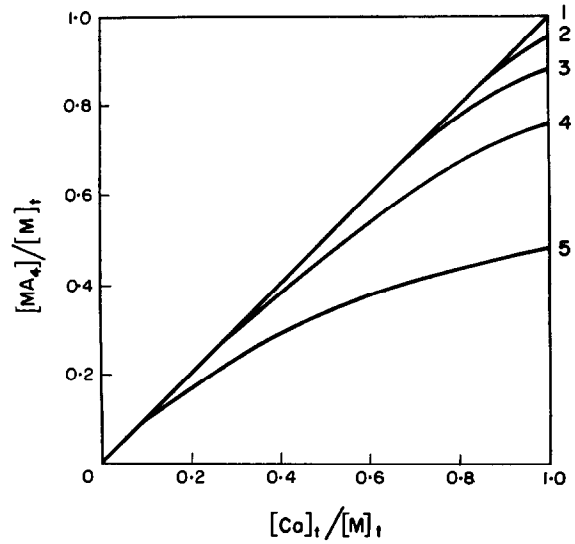


FIG. 1—$[MA_4]/[M]_t$ *versus* $[Ca]_t/[M]_t$.
$K_1[A]^4$: (1) 10^4, (2) 10^3, (3) 10^2, (4) 10, (5) 1.

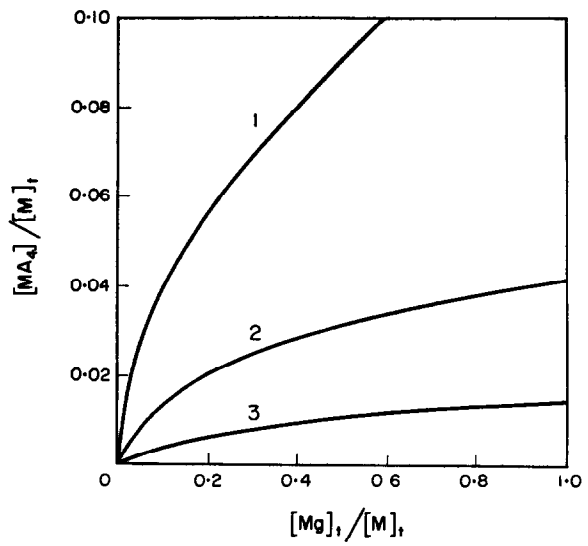


FIG. 2—$[MA_4]/[M]_t$ *versus* $[Mg]_t/[M]_t$.
$K_1'[A]^4$: (1) 10^{-2}, (2) 10^{-3}, (3) 10^{-4}.

$K_{Ca-EGTA}/K_{Mg-EGTA}(10^{5\cdot8})$ is much greater than $K_{Ca-EDTA}/K_{Mg-EDTA}(10^{2\cdot0})$, and one can realise $K_1[A]^4$ higher than 10^2 together with $K_1'[A]^4$ lower than 10^{-3} in an exchange equilibria in which EGTA participates.

Choice of M

It is preferable that M gives a well-defined polarogram under the given conditions. Moreover, K_{MY}, K_{MA_4} and the rate of exchange reaction (1) must be taken into consideration. Elements such as copper, zinc, cadmium, nickel and cobalt are known to form more or less stable ammine complexes. Among them only zinc and cadmium give a one-step reduction wave in an ammonia-ammonium chloride supporting electrolyte and their rate of exchange reaction (1) is sufficiently fast. Thus it is convenient to confine our considerations to the cases of zinc and cadmium.

The stability constants of the species concerned are:[4-6]

$\log K_{Ca-EGTA}$: 11·0 $\log K_{Mg-EGTA}$: 5·2

$\log K_{Zn-EGTA}$: 12·8 $\log K_{Cd-EGTA}$: 16·7

$\log K_{Zn(NH_3)_4}$: 9·58 $\log K_{Cd(NH_3)_4}$: 7·0.

Using these constants $K_1[A]^4$ and $K_1'[A]^4$ can be calculated for various concentrations of ammonia. The results are tabulated in Table I.

TABLE I—CALCULATED VALUES OF LOG $K_1[A]^4$ AND LOG $K_1'[A]^4$ FOR VARIOUS CONCENTRATIONS OF AMMONIA

$[NH_3]$, *M*	Zn-EGTA		Cd-EGTA	
	$\log K_1[A]^4$	$\log K_1'[A]^4$	$\log K_1[A]^4$	$\log K_1'[A]^4$
2·0	8·8	3·0	2 5	−3·3
1·0	7·6	1 8	1 3	−4·5
0·5	6 4	0 6	0 1	−5 7
0·1	3 6	−2 2	−2 7	−8 5

In the case of Zn–EGTA, $K_1[A]^4$ is so high even in 0·1*M* ammonia solution, that it is difficult to get a sufficiently low value of $K_2[A]^4$ because $K_1/K_2 = K'_{Ca-EGTA}$. Thus (4) does not hold for a wide range of $[Ca]_t/[Zn]_t$. On the other hand, $K_1'[A]^4$ cannot be sufficiently low under such conditions, as seen from the relationship $K_1/K_1' = K_{Ca-EGTA}/K_{Mg-EGTA}$. This is why the effect of magnesium can hardly be neglected in the case of Zn–EGTA. Though $K_2[A]^4$ and $K_1'[A]^4$ become fairly low in more dilute ammonia solutions ($<0{\cdot}1M$), it is not possible to obtain a well-defined wave of zinc ammine complex in such solutions.

In the case of Cd–EGTA, on the contrary, the circumstances are much more favourable, because $K_{Cd-EGTA} > K_{Zn-EGTA}$ and $K_{Cd(NH_3)_4} < K_{Zn(NH_3)_4}$. One can thus easily realise a sufficiently high value of $K_1[A]^4$ together with a sufficiently low value of $K_1'[A]^4$ in 0·5–1*M* ammonia solution. From the practical point of view, the use of cadmium seems to be advantageous for the following reasons:

1. The cadmium ammine complex gives a reduction wave at a potential less negative than that of the zinc ammine.

2. Because of the ease of reversibility of the reduction of the cadmium ammine complex, it would be possible to realise higher sensitivity with the aid of square wave polarography.

EXPERIMENTAL

Reagents

$10^{-1}M$ EGTA *solution* Twenty ml of $1N$ sodium hydroxide solution are added to 3·8036 g of the pure reagent (Dojin Chemical Co , Kumamoto, Japan) and the whole is diluted to 100 ml. The solution is standardised chelatometrically with cadmium standard solution using Erio T as indicator.

$1\ 04 \times 10^{-1}M$ *Zinc solution* 0 6808 g of metallic zinc (99 99%) is dissolved in a small amount of hydrochloric acid. The excess acid is expelled by evaporation and the solution diluted to 100 ml.

$1\ 04 \times 10^{-1}M$ *Cadmium solution* 1 169 g of metallic cadmium (99·99%) is dissolved in a small amount of hydrochloric acid. The same procedure is then followed as for the zinc solution

Metal-EGTA solution· Equivolume mixtures of the preceding solutions give a $5 \times 10^{-2}M$ metal-EGTA solution containing a slight excess of metal

$10^{-2}M$ *Calcium standard solution*· 1,000 g of calcium carbonate (G P) is dissolved in a small amount of hydrochloric acid and carbon dioxide is expelled by boiling. The whole is diluted to 1 litre. The solution is standardised chelatometrically.

10^{-2} *and* $10^{-1}M$ *Magnesium standard solution*· Magnesium chloride (G P.) is dissolved in water and the solution is standardised chelatometrically.

0 2% *Gelatine solution* Prepare daily.

Apparatus

Pen-recording polarograph (Yanagimoto Co. Ltd , Kyoto, Japan); Characteristics of the dropping mercury electrode: m = 1 42 mg/sec, t = 6 4 sec (open circuit).

Trial procedure

Calcium and/or magnesium solution and 1 0 ml of 0 2% gelatine solution are added to a 10-ml volumetric flask containing 1 ml of $5 \times 10^{-2}M$ metal-EGTA solution, 1–2 ml of $1{\cdot}0M$ ammonium chloride solution and various amounts of $8{\cdot}0M$ ammonia solution The solution is then diluted to the mark An aliquot of the solution is transferred to the polarographic cell. Dissolved oxygen is expelled by a stream of nitrogen passed through an ammonia solution of the same concentration as the electrolytic solution The polarogram of zinc or cadmium ammine is finally recorded

Recommended Procedure

The sample solution should preferably contain 5–20 mg of magnesium and less than 1 mg of calcium in 1–2 ml One–two ml of sample solution are added to a 10-ml volumetric flask containing 1 ml* of $5 \times 10^{-2}M$ Cd-EGTA solution, 1 ml of $1{\cdot}0M$ ammonium chloride solution and 1 ml of $5{\cdot}0M$ ammonia solution † After 1 ml of 0 2% gelatine solution is added, the whole is diluted to the mark. Oxygen is expelled by a stream of nitrogen passed through a $0{\cdot}5M$ ammonia solution The polarogram is recorded between −0 5 and −1·0 V. The same procedure is followed on a solution containing 5–20 mg of magnesium and no calcium. The difference in wave-heights between the two measurements may be attributed to the cadmium ammine complex produced by calcium. Consulting a previously constructed calibration curve, one finds the amount of calcium in the sample solution.

RESULTS AND DISCUSSION

The relationship between wave-height and calcium or magnesium concentration was examined for various concentrations of ammonia and the results are summarised in Figs. 3–6. These results verify the previous considerations. In the case of Zn–EGTA, a linear relationship is observed between $[Ca]_t$ and the wave-height of the zinc ammine complex when the ammonia concentration is higher than $0{\cdot}06M$. However, in these solutions zinc ammine produced by magnesium cannot be neglected (see Fig. 4). Though the effect of magnesium may be neglected in more dilute ammonia solutions, zinc does not give a well-defined polarogram in these solutions.

* The amount of Cd-EGTA should be more than twice as large as the expected amount of calcium on an equivalence basis.

† If the sample solution contains free base or acid in appreciable amount, it must be taken into consideration.

In the case of Cd–EGTA, a linear relationship holds between $[Ca]_t$ and the wave-height of the liberated cadmium ammine complex in the following range: 0–4 $\times 10^{-3}M$ of $[Ca]_t$, i.d. 0–0·8 $[Ca]_t/[Cd]_t$, in $1M$ ammonia solution and 0–3 $\times 10^{-3}M$ of $[Ca]_t$, i.d. 0–0·6 $[Ca]_t/[Cd]_t$ in $0{\cdot}5M$ ammonia solution (Fig. 5). As

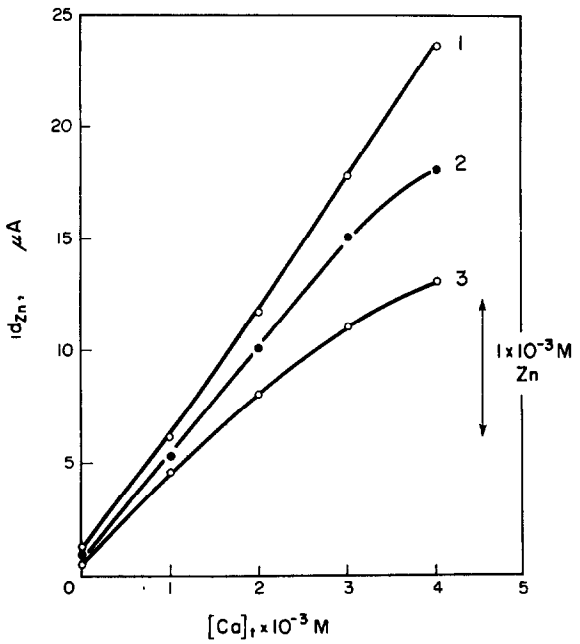


FIG 3—i_{dZn} *versus* $[Ca]_t$
Total concentration of EGTA: 4·71 $\times 10^{-3}M$; total concentration of zinc: 4·80 $\times 10^{-3}M$; NH_4Cl: 0·1M; gelatine: 0·02%; NH_3 concentration: (1) 0·06–0·08M, (2) 0·03M, (3) 0·02M.

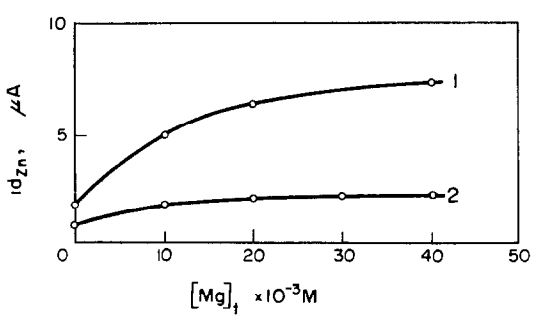


FIG 4—i_{dZn} *versus* $[Mg]_t$
Total concentration of EGTA: 4·71 $\times 10^{-3}M$; total concentration of zinc. 4·80 $\times 10^{-3}M$, NH_4Cl: 0·2M, gelatine: 0·02%; NH_3 concentration: (1) 0·08M, (2) 0·04M.

seen from Fig. 6, in 0·5–1·0M ammonia solutions very little effect from magnesium is observed. Particularly in 0·5M ammonia, the effect of magnesium may be neglected even if the concentration attains $10^{-1}M$ ($[Mg]_t/[Cd]_t = 20$). Thus one may choose

any concentration of ammonia between 0·5 and 1·0*M* according to the expected concentration of calcium and magnesium in the sample solution.

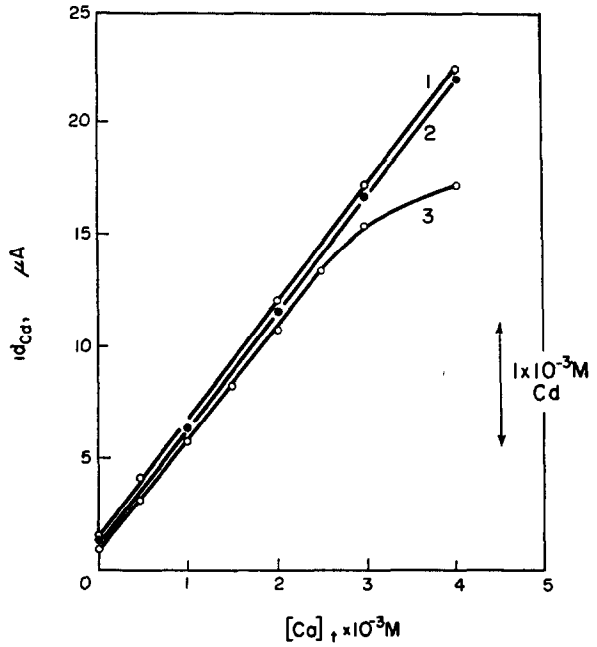


FIG 5—i_{dCd} *versus* $[Ca]_t$
Total concentration of EGTA: 4 89 × 10^{-3}*M*; total concentration of cadmium: 4 98 × 10^{-3}*M*; NH_4Cl: 0 1*M*; gelatine: 0·02%; NH_3 concentration: (1) 1·6*M*, (2) 1 0*M*, (3) 0·5*M*.

In Fig. 6 it is shown that the higher the magnesium concentration, the smaller is the value $\Delta i_{dcd}/\Delta[Mg]_t$ (i.d. $\Delta[Cd(NH_3)_4]/\Delta[Mg]_t$). Therefore, when one deals with a sample containing a large amount of magnesium, it may be convenient to minimise its effect by adding magnesium in an amount 10–20 times* as much as

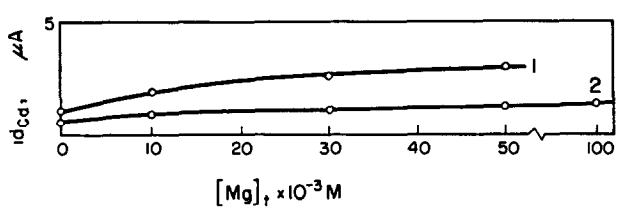


FIG 6—i_{dCd} *versus* $[Mg]_t$
Total concentration of EGTA: 4·89 × 10^{-3}*M*; total concentration of cadmium: 4 98 × 10^{-3}*M*; NH_4Cl: 0·2*M*; gelatine: 0·02%; NH_3 concentration: (1) 1·0*M*, (2) 0·5*M*

calcium and subtracting the wave-height of the blank solution† from the resulting wave-height. Thus it is possible to determine calcium accurately in mixtures containing a large excess of magnesium (*cf.* Table II).

* The effect of magnesium not being considerable, one need not necessarily add exactly the same amount of magnesium as in the sample solution (*cf.* Fig. 6).

† This solution is composed of no calcium and *about* the same amount of magnesium as in the preceding solution.

TABLE II—DETERMINATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM

Ca taken, *mg*	Mg taken, *mg*	Mg/Ca (atomic ratio)	Ca found, *mg*	Diff., *mg*
0 20	0	0	0 19	−0 01
			0 20	0
	0 25	2	0 19	−0·01
	2·5	20	0 21	+0 01
	5 0	40	0 22	+0 02
0 40	0 25	1	0·39	−0 01
	2 5	10	0 40	0
	10	40	0·42	+0 02
	10	40	0·45[a]	+0 05
0 80	2 5	5	0 79	−0 01
	10	20	0 82	+0·02
1 20	2·5	3 3	1·16	−0 04
	7 5	10	1·21	+0 01
	10	13 3	1 20	0

[a] No magnesium was added to the blank solution.

Taking into account these considerations, the *Recommended Procedure* for the selective determination of calcium in the presence of magnesium was finally adopted.

In Fig. 7 the influence of magnesium on the determination of calcium is shown. As seen from the results given in Table II, submilligram quantities of calcium can be determined in the presence of a large amount of magnesium.

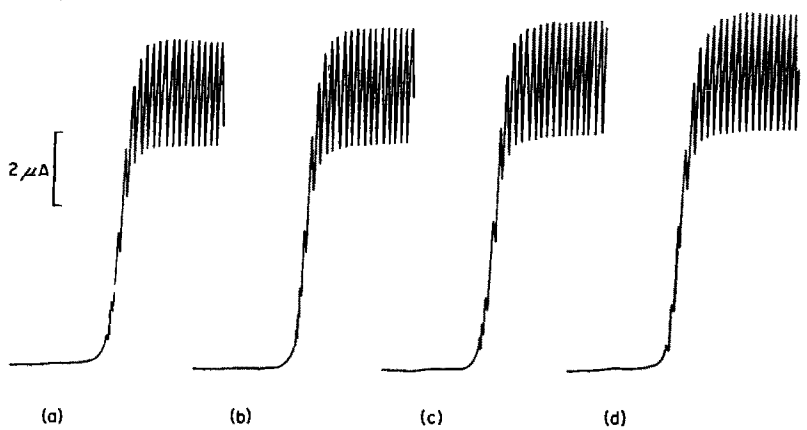


FIG 7—Influence of magnesium on the determination of calcium.
Total concentration of EGTA $4{\cdot}89 \times 10^{-3}M$; total concentration of cadmium: $4{\cdot}98 \times 10^{-3}M$; NH_4Cl: $0{\cdot}2M$; NH_3: $0{\cdot}5M$; gelatine: 0·02%; calcium added: $10^{-3}M$; magnesium added. (a) $0M$, (b) $10^{-2}M$, (c) $5 \times 10^{-2}M$, (d) $10^{-1}M$.

Stability constants of Zn–EGTA and Cd–EGTA

Because the values of $K_{Ca-EGTA}$, $K_{Mg-EGTA}$, $K_{Zn(NH_3)_4}$ and $K_{Cd(NH_3)_4}$ are known, equations (3) and (5) enable one to calculate the stability constants of Zn–EGTA and Cd–EGTA provided the concentration of zinc and cadmium ammines can be determined experimentally.

A linear relationship between the limiting current and square root of mercury head confirms that the observed waves are diffusion-controlled. Thus it may be considered that the limiting current reflects the concentration of zinc or cadmium ammine complex.

The results are tabulated in Table III. The constancy of these values confirms the validity of our earlier considerations. These values compare favourably with those obtained by previous workers.[5]

TABLE III—STABILITY CONSTANTS OF Zn-EGTA AND Cd-EGTA (AT 20 ± 1°)

1 Zn-EGTA

Conditions	Mg added ($\times 10^{-3}M$)	$Zn(NH_3)_4$ produced ($\times 10^{-3}M$)	log $K_{Zn-EGTA}$
0·5M NH_3 0·2M NH_4Cl 5 × $10^{-3}M$ in Zn-EGTA	5 0 10 0	1·20 1 61	$12\ 5_5$ $12\ 8_3$

Conditions	Ca added ($\times 10^{-3}M$)	$Zn(NH_3)_4$ produced ($\times 10^{-3}M$)	log $K_{Zn-EGTA}$
0 02M NH_3 0·1M NH_4Cl 5 × $10^{-3}M$ in Zn-EGTA	2 0 4 0	1 89 2 65	$12\ 7_3$ $12\ 7_8$

2 Cd-EGTA

Conditions	Mg added ($\times 10^{-3}M$)	$Cd(NH_3)_4$ produced ($\times 10^{-3}M$)	log $K_{Cd-EGTA}$
0 5M NH_3 0 2M NH_4Cl 5 × $10^{-3}M$ in Cd-EGTA	10 0 100 0	$0\ 05_0$ $0\ 11_1$	$15\ 0_2$ $15\ 5_0$
1 0M NH_3 0 2M NH_4Cl 5 × $10^{-3}M$ in Cd-EGTA	10 0 30 0 50 0	$0\ 12_6$ $0\ 22_6$ $0\ 30_8$	$15\ 6_9$ $15\ 6_5$ $15\ 6_1$

Conditions	Ca added ($\times 10^{-3}M$)	$Cd(NH_3)_4$ produced ($\times 10^{-3}M$)	log $K_{Cd-EGTA}$
0 5M NH_3 0 1M NH_4Cl 5 × $10^{-3}M$ in Cd-EGTA	35 0 40·0	2 95 3 26	$15\ 8_9$ $15\ 8_4$

Zusammenfassung—Man betrachtet das Austauschgleichgewicht:

$$MY + Ca + nNH_3 \rightleftharpoons M(NH_3)_n + CaY$$

um eine gunstigen Bedingungen fur die polarographischen Indirektbestimmung des Calciums zu finden Es wird die Benutzung von Cd-ÄGTA vorschlagen fur die selektiven Bestimmung des Calciums im Gegenwart eines grosses Überschusses des Magnesiums.

Résumé—Pour trouver une condition optima pour le dosage polarographique indirect du calcium, la considération quantitative est faite sur l'équilibre d'échange suivant

$$MY + Ca + nNH_3 \rightleftharpoons M(NH_3)_n + CaY$$

On propose l'emploi de Cd-EGTA pour le dosage selectif du calcium en présence d'un grand excès de magnésium.

REFERENCES

[1] R Přibil and E. Vicenová, *Coll. Czech. Chem. Comm*, 1953, **18**, 308.
[2] R. Přibil and Z Roubal, *ibid*, 1954, **19**, 252.
[3] G Nakagawa and M. Tanaka, *Talanta*, in press.
[4] G. Schwarzenbach, *Die komplexometrischen Titration*. Dritte Auflage, Ferdinand Enke Verlag, Stuttgart, 1957, p 97
[5] A Ringbom, G. Pensar and E Wänninen, *Anal Chim. Acta*, 1958, **19**, 525.
[6] J Bjerrum, G Schwarzenbach and L G Sillén, *Stability Constants*, Part II. The Chemical Society, 1958

Talanta, 1962, Vol 9, pp 857 to 862 Pergamon Press Ltd Printed in Northern Ireland

POTENTIOMETRIC DETERMINATION OF VANADIUM^{IV} WITH CERIUM^{IV} SULPHATE AT ROOM TEMPERATURE

SIMULTANEOUS DIFFERENTIAL POTENTIOMETRIC TITRATION OF IRON^{II} AND VANADIUM^{IV} AT ROOM TEMPERATURE

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Summary—The use of orthophosphoric acid as a catalyst has enabled the potentiometric titration of vanadium^{IV} to be carried out with cerium^{IV} sulphate in 1·0–2·0*N* sulphuric acid medium at room temperature. Using the same catalyst a method has also been developed for the simultaneous differential potentiometric titration of iron^{II} and vanadium^{IV} with cerium^{IV} sulphate in a sulphuric acid medium; this method is more satisfactory than the procedure described by Furman[1] because the first potential break is quite marked and it is more convenient because it avoids the high temperature required for the second stage of the titration in the Furman procedure. Chromium^{III} and iron^{III} do not interfere in these titrations.

FURMAN[1] attempted the potentiometric determination of vanadium^{IV} in sulphuric acid medium with cerium^{IV} sulphate. When the titration was carried out at room temperature, he observed that it required several min for the potential to become constant in the neighbourhood of the equivalence point and therefore recommended the titration to be carried out at 50–60°. He observed that the potential break at the equivalence point varied from 25 to 100 mv per 0·05 ml of 0·05*N* cerium^{IV} solution when the initial volume of the titration mixture was varied from 200 to 25 ml. Almost simultaneously Willard and Young[2] reported that vanadium^{IV} can be determined potentiometrically at 70–75° with cerium^{IV} sulphate in sulphuric, hydrochloric or perchloric acid media.

We have observed that potentiometric titrations in 0·5 to 2·0*N* hydrochloric acid medium give much higher titres than the theoretical, the error increasing with increasing concentration of hydrochloric acid. During the earlier part of the titration the potential rises, then remains steady for a long interval until the equivalence point is passed when the potential shows a sudden jump. We[3] have shown that the need for a high temperature arises from the fact that the reaction between vanadium^{IV} and cerium^{IV} is slow in a sulphuric acid medium at room temperature. Various catalysts were tried to see if the reaction could be accelerated sufficiently well to enable the titration to be carried out at room temperature and it was found that orthophosphoric acid has a pronounced accelerating effect on the reaction. This observation has now been utilised for the potentiometric determination of vanadium^{IV} with cerium^{IV} sulphate at room temperature and for the differential potentiometric titration of iron^{IV} and vanadium^{IV} in mixtures.

EXPERIMENTAL

Reagents

Iron^{II} ammonium sulphate solution, approx. 0·05*N* Prepared by dissolving about 20 g of the substance in 1 litre of water, sufficient sulphuric acid being added before dilution to give an overall acidity of 1·0*N* The solution is standardised against cerium^{IV} sulphate solution.

The preparation of 0·05*N* cerium^{IV} sulphate and 0·05*N* vanadium^{IV} sulphate solutions and the source of phosphoric acid have already been described.[3]

Apparatus

The potentiometric titration assembly consisted of a Junior potentiometer and a Taut suspension galvanometer (both manufactured by W. G. Pye & Co., England), a saturated calomel electrode as reference electrode and a bright platinum rod electrode as indicator electrode The salt bridge consisted of a U-tube (with porous end plates) filled with saturated potassium chloride solution. The titration mixture was stirred during the titration by means of a B T L. magnetic stirrer.

RESULTS AND DISCUSSION

About 5·0 ml of 0·05*N* vanadium^{IV} solution is taken in a 150-ml Pyrex beaker and diluted to 80 ml with 1·0*N* sulphuric acid. When the mixture is titrated at room temperature (28°), the potentials attain stable values quickly after each addition of the cerium^{IV} sulphate solution in the initial stages. As the equivalence point is approached, however, the potentials show considerable drift with time, reaching steady values in about 3 min, then just before the equivalence point, it takes 4 min for the potential to reach a constant value. After the equivalence point is reached, the potentials again attain steady values quickly. This behaviour is exemplified by the results presented in Table I. The results also show that in the presence of phosphoric acid (1·0 ml of syrupy phosphoric acid for 80 ml of titration mixture) the potentials do not show any drift with time even in the neighbourhood of the equivalence point.

TABLE I.—POTENTIOMETRIC TITRATION OF VANADIUM^{IV} WITH CERIUM^{IV} SULPHATE AT ROOM TEMPERATURE (28°)

Volume of cerium^{IV} sulphate added, *ml*	Addendum	e m f (v) observed after							
		30 sec	60 sec	90 sec	120 sec	150 sec	180 sec	210 sec	240 sec
5·70	Nil	0 869	0 867	0 866	0 865	0 865	0 865	—	—
	1 0 ml of H_3PO_4	0 864	0 864	0·864	—	—	—	—	—
5 80	Nil	0 905	0 885	0 881	0 880	0 880	0 880	—	—
	1 0 ml of H_3PO_4	0 879	0 877	0 877	0 877	0 877	—	—	—
5 90	Nil	0 960	0 950	0 945	0 930	0 927	0 920	0 914	0 911
	1 0 ml of H_3PO_4	0 907	0 904	0 904	0 904	0 904	—	—	—
6 00	Nil	1 081	1 080	1 080	1 080	1 080	1·080	—	—
	1 0 ml of H_3PO_4	1 004	1 004	1 004	1 004	1 004	1 004	—	—
6 10	Nil	1 127	1 128	1 128	1 128	—	—	—	—
	1 0 ml of H_3PO_4	1 075	1 075	1 075	—	—	—	—	—

5 0 ml of vandium^{IV} solution ≡ 5 98 ml of cerium^{IV} sulphate solution

The value of the potential break obtained in a titration carried out (in the presence of phosphoric acid) at room temperature is about 20 mv lower than the potential break obtained during a titration carried out at 60° in the absence of phosphoric acid. This is evident from the data in Table II.

Although the potential break in the presence of phosphoric acid is lower than that obtained in its absence, the potential break is still sufficiently high to enable the equivalence point to be detected easily. The potential break increases as the sulphuric

acid concentration decreases, but there is a risk of cerium phosphate being precipitated when the concentration of sulphuric acid is below 1·0*N*. Several titrations of vanadium^{IV} have also been carried out keeping the concentration of sulphuric acid at 2·0*N*, but varying the amount of syrupy phosphoric acid from 0·5 to 2·5 ml. The results in Table III show that the potential break decreases as the phosphoric acid concentration increases. Moreover, when the amount of syrupy phosphoric acid is increased beyond 2·5 ml precipitation of cerium phosphate begins. In view of these findings, the optimum amount of syrupy phosphoric acid is fixed as

TABLE II

Conditions of titration	Potential break at the equivalence point per 0 1 ml of 0 04*N* cerium^{IV} sulphate, *mV*
0 5*N* H_2SO_4 at 60°	153
0 5*N* H_2SO_4 + 1 0 ml of H_3PO_4 at 28°	129
1 0*N* H_2SO_4 at 60°	147
1 0*N* H_2SO_4 + 1 0 ml of H_3PO_4 at 28°	108
2 0*N* H_2SO_4 at 60°	107
2 0*N* H_2SO_4 + 1 0 ml of H_3PO_4 at 28°	96

1·0 ml for 80 ml of the titration mixture and the optimum concentration of sulphuric acid prescribed as 1·0 to 2·0*N*. When 5·0 ml of syrupy phosphoric acid is used, the titration can be made in 4·0*N* sulphuric acid medium without any risk of cerium phosphate being precipitated. The potential break under these conditions is 84 mv per 0·1 ml of 0·04*N* cerium^{IV} solution as compared with the break of 96 mv obtained in titrations in 2·0*N* sulphuric acid (using 1·0 ml of syrupy phosphoric acid) and a break of 108 mv observed in titrations in 1·0*N* sulphuric acid (using 1·0 ml of syrupy phosphoric acid). These results can be understood when we take into account the facts that the vanadium^{V}/vanadium^{IV} potential increases with increase in the acid concentration, and that the cerium^{IV}/cerium^{III} potential does not change very much with an increase in the concentration of sulphuric acid.

TABLE III —EFFECT OF PHOSPHORIC ACID ON THE POTENTIOMETRIC TITRATION OF VANADIUM^{IV} WITH CERIUM^{IV} SULPHATE IN 2·0*N* SULPHURIC ACID AT ROOM TEMPERATURE

Amount of phosphoric acid added, *ml*	Break in potential at the equivalence point per 0 10 ml of 0 04*N* cerium^{IV} sulphate, *mV*
0 50	109
1 00	96
2·50	91

Recommended procedure for potentiometric titration of vanadium^{IV} with cerium^{IV} sulphate

An aliquot volume of vanadium^{IV} solution taken in a 150-ml Pyrex beaker is diluted to 80 ml with 1 0 to 2·0*N* sulphuric acid, then treated with 1 0 ml of syrupy phosphoric acid The titration is carried out with 0 05*N* cerium^{IV} sulphate solution using the electrometric titration assembly described above The cerium^{IV} sulphate is added while stirring the solution and the stirring is continued for about 15 sec after each addition. The stirring is then stopped and the potential noted. Towards the close of the titration, the potentials are noted 1 min after each addition of cerium^{IV} sulphate The break in potential at the end-point per 0 05 ml of 0 05*N* cerium^{IV} sulphate corresponds to about 50–60 mv.

Some typical results are given in Table IV.

TABLE IV

Amount of vanadium^{IV}, *millimoles*	
Taken	Found
0 3030	0 3018
0 3310	0 3315
0 4417	0 4402
0 6061	0 6046
1 0200	1·0170

Interferences

Iron^{III} and chromium^{III} do not interfere with the determination of vanadium^{IV} by the proposed method. The presence of these salts does not even effect the value of the break in potential.

Titration in a hydrochloric acid medium

Titration of vanadium^{IV} with cerium^{IV} sulphate in hydrochloric acid medium at room temperature using phosphoric acid as a catalyst gave slightly higher titres than the theoretical values (about 1·5% higher in 1·0*N* hydrochloric acid and 2·0% higher in 2·0*N* hydrochloric acid).

Titration in a perchloric acid medium

In the titration of vanadium^{IV} with cerium^{IV} sulphate solution in 0·5 to 2*N* perchloric acid medium the potential jumps are higher than in a sulphuric acid medium, but the titres are still slightly higher (about 0·5 to 1·0%) than the theoretical values.

Differential titration of iron^{II} and vanadium^{IV} in mixtures

Furman[1] reported the potentiometric titration of a mixture of iron^{II} and vanadium^{IV} with cerium^{IV} sulphate in the following manner. The mixture is first titrated at room temperature, then at 50–60°. The first jump in potential corresponds to complete oxidation of iron^{II} and the second jump corresponds to complete oxidation of vanadium^{IV}. The method is not satisfactory because the first jump in potential is very small. The correct equivalence point corresponding to the complete oxidation of iron^{II} can be obtained only from the curve showing the relation between $\frac{\Delta E}{\Delta V}$ and V. The equivalence point cannot be obtained from the simple curve showing the relation between E and V. Smith and Getz[4] carried out the differential potentiometric titration of a mixture of iron^{II} and vanadium^{IV} perchlorates in 8*N* perchloric acid medium with ammonium nitratocerate. They found that the potential break at either of the stages is about 300 mV. Obviously this method is not of much practical interest because it would be very tedious indeed to get both of the metals in the form of perchlorates.

We have been able to carry out the simultaneous differential titration of iron^{II} and vanadium^{IV} in 1·0–2·0*N* sulphuric acid medium at room temperature using a small quantity of orthophosphoric acid as a catalyst for the oxidation of vanadium^{IV} by cerium^{IV}.

When a mixture of iron^{II} and vanadium^{IV} is titrated with cerium^{IV} sulphate, iron^{II} will be oxidised first and even if a little vanadium^{IV} is oxidised, the vanadium^{V} formed will, in turn, oxidise iron^{II} and itself be reduced to vanadium^{IV}, so that in effect vanadium^{IV} will not be oxidised until iron^{II} is completely oxidised. After all of the iron^{II} is oxidised the slight excess of cerium^{IV} oxidises vanadium^{IV} to vanadium^{V} and there will be a sudden jump in potential. This break in potential corresponds to the one obtained during the electrometric titration of iron^{II} with vanadium^{V}. Moreover, the presence of phosphoric acid helps to increase the value of this break in potential; under our experimental conditions the first break has been found to have a value of 60–70 mv per 0·05 ml of 0·05*N* cerium^{IV} sulphate solution. The second break in potential has been observed to have a value of 55–65 mv per 0·05 ml of 0·05*N* cerium^{IV} sulphate solution.

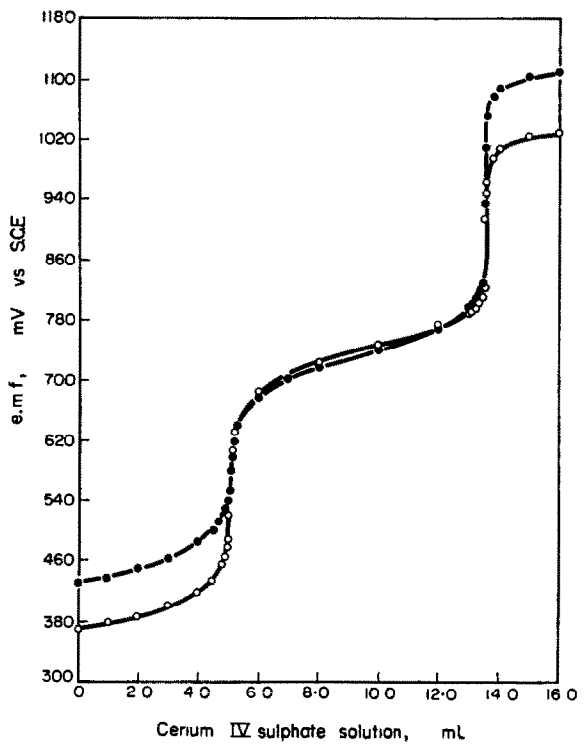


FIG. 1.—Electrometric titration of a mixture of iron^{II} and vanadium^{IV} with cerium^{IV} sulphate:
●—1·0*N* sulphuric acid, according to Furman's procedure
○—1·0*N* sulphuric acid in the presence of 1 ml of phosphoric acid, at room temp.

Recommended procedure for potentiometric titration of a mixture of iron^{II} and vanadium^{IV} with cerium^{IV} sulphate

The mixture of iron^{II} and vanadium^{IV} taken in a 150-ml Pyrex beaker is diluted with 1·0–2·0*N* sulphuric acid to 50 ml and 1·0 ml of syrupy phosphoric acid is added. It is then titrated with cerium^{IV} sulphate solution at room temperature using the potentiometric equipment already described.

Some typical results are presented in Table V.

Fig. 1 gives a typical curve showing the relation between the observed e.m.f. and the volume of cerium^{IV} sulphate solution added. The results show that the method now

developed is precise and more convenient than those of previous investigators. The method is likely to prove of great value in the analysis of vanadium steels and chrome vanadium steels.

We have attempted to use ferroin in the phosphoric acid catalysed system. If the titration is made in a 1·0*N* sulphuric acid medium the indicator shows the colour change when both iron^{II} and vanadium^{IV} are oxidised, but the colour transition is not sharp on account of the diminishing intensity of the ferroin red colour as the end-point is approached. This determination can be made very satisfactorily by carrying out

TABLE V

Amount of iron^{II}, *millimoles*		Amount of vanadium^{IV}, *millimoles*	
Taken	Found	Taken	Found
0 2939	0 2947	0 3988	0 3988
0 3000	0 2996	0 5000	0 4983
0 3515	0 3530	0 3843	0 3843
0 4000	0 3985	0 4000	0 3985
0 6000	0 5991	0 4000	0 3992

the titration in a 1·5–2·5*N* sulphuric acid medium using Rhodamine 6G as a fluorescence indicator, in the presence of 1·0–1·5 ml of syrupy phosphoric acid per 50 ml of the titration mixture. Iron^{II} alone can be determined by carrying out the titration with cerium^{IV} sulphate in 10–12*N* sulphuric acid, because any vanadium^{V} formed by oxidation of vanadium^{IV} will oxidise ferroin in 10–12*N* sulphuric acid.

Zusammenfassung—Die Verwendung von Phosphorsaure als Kalalysator ermoglicht die potentiometrische Titration von Vanadin(IV) mit Cer(IV) in 1–2 n Schwefelsaure bei Zimmertemperatur Mit dem gleichen Katalysator wurde ein Methode entwickelt zur simultanen, differential-potentiometrischen Titration von Eisen(II) und Vanadin-(IV) mit Cer(IV) in schwefelsaurem Medium. Diese Methode arbeitet besser als die von Furman, da der erste Potentialsprung besser ausgepragt ist. Ein weitere Vorteil ist, dass fur den zweiten Teil der Titration keine erhohte Temperatur benotigt wird Chrom(III) und Eisen(III) storen nicht

Résumé—L'utilisation de l'acide orthophosphorique comme catalyseur permet le titrage potentiométrique du vanadium(IV) par le sulfate de cérium(IV) en milieu acide sulfurique 1,0 à 2,0 N, à la température ordinaire En utilisant le même catalyseur, une méthode est proposée pour le titrage simultané par potentiométrie différentielle du fer(II) et du vanadium(IV) par le sulfate de cérium(IV) en milieu acide sulfurique; cette méthode est meilleure que celle de Furman pour deux raisons. le premier saut de potentiel est plus marqué et, de plus, la méthode est d'une mise en oeuvre plus commode en n'imposant pas d'opérer à haute température pour la deuxième partie du titrage Le chrome(III) et le fer(III) ne gênent pas dans ces dosages

REFERENCES

[1] N H. Furman, *J Amer Chem Soc*, 1928, **50**, 1675.
[2] H H Willard and P Young, *Ind Eng Chem*, 1928, **20**, 972
[3] G Gopala Rao and L S A Dikshitulu, *Talanta*, 1962, **9**, 289
[4] G. F. Smith and C A. Getz, *Ind Eng Chem*, *Analyt*, 1938, **10**, 191

Talanta, 1962, Vol 9, pp 863 to 865 Pergamon Press Ltd Printed in Northern Ireland

BOOK REVIEWS

Instrumental Methods for the Analysis of Food Additives. WILLIAM H BUTZ and HENRY J. NOEBELS. Interscience Publishers, New York, 1961. pp. viii + 288. $11.

THIS volume is the published proceedings of a Symposium held in Michigan State University during March, 1960. The Symposium, which was attended by Food Chemists and Biologists from a wide field, was initiated following the invoking of the new U.S. food laws. Under these laws the burden of proving the safety of additives rests with the food processor The editors of the book (both employees of Beckman Instruments Inc.) claim that it comprises "a comprehensive review of low level analysis including specific, fast and reliable procedures both new and old "

The first part of the book is devoted to the significance of the new food laws and the way in which they operate in practice It describes the petition that the manufacturer must make to the F D.A. and the safeguards required by that organisation before an additive is likely to be considered as acceptable It also describes the recourse which the petitioner has should his proposal be rejected. It is pointed out that it is a matter of opinion as to whether the biological knowledge of today is totally adequate to support legislation designed to provide complete safety in the use of these chemicals, and that the case for allowing finite amounts of specified chemicals in certain foodstuffs becomes unassailable if the populations of the world are to be fed in adequate quantities

The second part of the book deals with analytical evaluation of additives in food. It reviews methods of sampling and the cleanup procedures advocated prior to final determination. Specifically referred to are the methods to be applied when determining DDT residues in many differing types of foodstuffs, and also of different residues which might be found in packaging materials.

The third part is concerned with identification and it is here that instrumentation is discussed in any detail. Amongst the instruments and techniques cited are those for (a) colorimetry, (b) ultraviolet spectrophotometry, (c) infrared spectroscopy, (d) isotope dilution technique, and (e) micro coulometric gas chromatography.

Part four is entitled "Analytical Procedures" and includes how to set up a food additives laboratory and what equipment is required. It includes certain specific methods, *e g* , quinine in tonic water, maleic hydrazide in potatoes, methylcellulose in mayonnaise, oleandomycin in animal feeds, Tween in ice cream, and gibberellic acid in beer.

The volume is of undoubted interest to food analysts everywhere, but my opinion is that the technique side of the problems is treated rather superficially and that the many snags which arise in applying methods to biological material are not given sufficient emphasis The problems are more difficult than the authors here imply.

R F MILTON

Treatise on analytical chemistry. A comprehensive account in three parts. Edited by I M. KOLTHOFF and PHILIP J ELVING, with the assistance of ERNEST B SANDELL. **Part II. Analytical chemistry of the elements. Section A. Systematic analytical chemistry of the elements. Volume I. Inorganic nomenclature. General concepts. Hydrogen. Water. Inert gases. Alkali metals.** Authors of Volume I: H F. BEEGHLY, GERHARD A COOK, W CONARD FERNELIUS, JAMES I HOFFMAN, SILVE KALLMAN, JOHN MITCHELL, JR. Interscience Publishers Inc , New York, Interscience Publishers Ltd , London, 1961 Pp xxi + 471, $16 00 (Subscription price $14 00)

THE aim of the textbook is to give a critical review of the methods of analytical chemistry rather than to be an encyclopædic work containing all methods of analysis General analytical methods, both classical and instrumental, have already been treated in Part I. Part II is being edited in three Sections; Section A deals with the analytical chemistry of the various elements, when present in inorganic substances; Section B will present the analysis of elements in organic substances, and Section C will deal with qualitative analysis, both inorganic and organic

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Talanta, 1962, Vol 9, pp 863 to 865 Pergamon Press Ltd Printed in Northern Ireland

BOOK REVIEWS

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complexes are dealt with It may be hoped that on this basis the nomenclature of complexes can be made uniform, since this field is at present somewhat of a jungle, because of the variety of names and concepts of nomenclature to be found in the literature.

In the short second part, *Determination of the Elements General Concepts*, James I Hoffman first presents an historical account of the tasks of analytical chemists, and then describes the difficulties and problems of analysts today and in the future

The systematic treatment of elements then begins. In all subsequent parts the material is arranged according to the following system: First a short summary is given of the occurrence of the element, of industrial processes involving it, and of its toxicology This introduction is followed by a description of analytically important physical and chemical properties of the element; distinctive features in the sampling of materials containing the element; an outline of its separation and isolation; systematic discussion of the current situation in respect of the detection and quantitative determination of the element and the analysis of its most important compounds, selected references for the determination of the element in specific materials; critically selected general laboratory procedures. The elements are in general arranged according to the Periodic Table.

The first systematically treated element is hydrogen (H F. Beeghly). Among methods of determination, the combustion method, the vacuum fusion method and the hot extraction method are detailed separately, while miscellaneous methods are mentioned briefly, with the corresponding references (11) in the bibliography.

Water is discussed in a separate section (John Mitchell, Jr.). For the detection of water four methods, and for its determination a wide range of methods, are described. Among chemical methods, the Karl Fischer titration is discussed in detail, but the acetyl chloride, acetic anhydride, calcium carbide, calcium hydride, magnesium nitride and other methods are also described. After discussion of gravimetric methods, and the separation of water, instrumental methods are described, including photometric and spectrometric, neutron-scattering, and other physical, thermal and electrical methods. The determinations of deuterium oxide and tritium oxide are presented in separate chapters. Recommended laboratory processes are summarised separately. An extensive bibliography, comprising 356 references, concludes this part.

The next part deals with the analytical chemistry of inert gases (Gerhard A Cook). Their isolation, and mass spectrometric methods, gas chromatography, emission spectroscopy, desorption methods and neutron-activation analysis are detailed. Analyses of binary mixtures by various physical methods are described. In addition to 129 original papers, a number of general references, including textbooks and monographs, are listed

The last part, dealing with the alkali metals (Silve Kallman) is arranged not according to the single elements, but according to methods; within these small chapters the methods for the determination of the alkali metals are detailed separately. Problems of sampling and qualitative tests are described thoroughly, and methods for the quantitative determination are presented in the following order: chemical methods, optical methods including flame photometry, polarographic procedures, radiochemical methods, stable isotope-dilution techniques. A separate chapter deals with the analysis of alkali metal alloys and compounds, selected laboratory processes are presented The Section concludes with 471 references.

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Although the book is written by a number of authors, each with experience in the appropriate field of analytical chemistry, the various parts are arranged fairly uniformly Thus, the user of the book can easily familiarise himself with the text When future volumes have been published, and the whole work is completed, analytical chemists will have an excellent guide in their work We await subsequent volumes with great interest

GYULA SVEHLA

Treatise on Analytical Chemistry. Edited by I. M Kolthoff and Philip J Elving, with the assistance of Ernest B. Sandell. **Part II. Analytical Chemistry of The Elements, Vol. 7.** Interscience Publishers, Inc , 1961, New York and London. Pp. xxiii + 567. Price $20.75; Subscription Price $18.50.

SECTION A of Part II of this treatise is concerned with the Systematic Analytical Chemistry of the Elements. The elements discussed in Volume 7 are sulphur (121 pp.) by B. J. Heinrich, M. D. Grimes, and J E. Puckett, selenium and tellurium (63 pp) by Thomas E Green and Max Turley; fluorine (105 pp.) by Charles A. Horton; chlorine, bromine, and iodine (80 pp.) by G. W. Armstrong, H. H. Gill, and R. F Rolf; manganese (70 pp.) by M. D. Cooper and Paul K. Winter; and rhenium (27 pp.) by Charles L. Rulfs. The chapters are organised according to the following outline: a brief discussion

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In general, the treatment of the elements in this volume is much more comprehensive than in earlier volumes. For example, the discussion of the analytical chemistry of sulphur is followed by 438 references. The material presented should surely be of interest and utility to all analysts The chapter devoted to selenium and tellurium features a knowledgeable discussion of the acidic character of these two elements and indicates a considerable amount of personal experience. There are no detailed laboratory procedures for these two elements, in the usual sense—an omission to be regretted in view of their unusual behaviour.

The chapter on fluorine is written by one who has been working in this field since his post-graduate days. As might be expected, the presentation of the material is both scholarly and comprehensive, and succeeded by 24 pages of references. Whereas most of the chapters are obviously reviews, the material on fluorine is based extensively on Dr. Horton's personal experience and evaluation.

The chapter devoted to the halogens is, in general, well presented, and is worthy of note by the analyst. It is marred, however, by several unusual and/or ambiguous statements, for example, "Since the most stable metal-to-halogen bonds are those that are most nearly covalent, the stability tends to shift preferentially to a reverse-order stability".

I found the chapter on manganese quite interesting and one of the most "readable" chapters in the series. The discussion of industrial processes involving manganese reveals a rather unusual personal knowledge of this facet.

Finally, the chapter on rhenium is very brief (as is also the material to be covered) but contains the essential information

In conclusion, there is no doubt that this volume represents a noticeable improvement over earlier volumes in the series.

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ERRATA—VOLUME 9

Page 706, *equations* (13) *and* (15) should read:

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Talanta, 1962, Vol 9, pp 867 to 868 Pergamon Press Ltd Printed in Northern Ireland

NOTICES

(Material for this Section should be sent directly to the Associate Editor)

CZECHOSLOVAKIA

November 1962: **Autumn Meeting:** *Association for Spectral Analysis.* Prague.

The *East Bohemia Section for Analytical Chemistry of ČSVTS* announces the **First International Exhibition of Photography in Microchemistry and Chemistry in Microphotography.** The purpose of the exhibition is to popularise micro methods in all branches of chemistry, preparative and analytical, and to make the public acquainted with the excellent work in this field. Everyone is welcome to participate in the exhibition with 4 black-and-white photographs (40 × 30 cm) and with 4 colour photographs (40 × 30 or 30 × 24 cm). On the reverse side of all photographs should be indicated the name of the author, his address and, if possible, the address of his employer and the description of the subject of the photograph. Material sent from abroad should be indicated by the following notice Photographs for exhibition—Unsaleable—Free of Duty Photographs will be accepted prior to 1 December, 1962

The exhibition will take place at Pardubice. The authors of the five best photographs will receive a Presentation Award Certificate. When the exhibition finishes, photographs will be returned to authors, although the organisers of the exhibition reserve for propagation the right to publish the photographs. Photographs should be sent by registered post to Dr. M VEČEŘA, výzkumný ústav organických syntéz, Pardubice, Rybitví, Czechoslovakia

DEUTSCHE DEMOKRATISCHE REPUBLIK

Die *Hauptjahrestagung* 1962 *der Chemischen Gesellschaft in der Deutschen Demokratischen Republik* findet in der Zeit von *Mittwoch, dem* 21. *November* 1962, *bis Sonnabend, dem* 24. *November* 1962, in Leipzig statt

Hauptthema **Methoden und Ergebnisse der Strukturchemie.**

SWEDEN

April 1964 **Third International Measurement Conference** (IMEKO) and **Sixth Instruments and Measurement Conference (I & M)** Stockholm.

As previously, the main purpose of the IMEKO Conference is to discuss the latest scientific achievements within fundamental and applied research from important branches of measurement and instrumentation The papers should deal with theory or practice of measurement and instrumentation of interest to the research scientist as well as to specialists engaged in the design and manufacture of instruments.

The Sections of the Conference, into which papers will be classified, are as follows

210 Fundamental problems of metrology
211 Theory and practice of instrument design
212 Technology and organisation in instrument manufacture.
213 General electronics as applied to measurements and instruments
214 Border-questions of measurement and automation
221. Instruments and methods for measuring geometrical and mechanical quantities, including geodetic measurements
223. Instruments and methods for measuring thermal quantities
224 Instruments and methods for physico-chemical measurements
225 Instruments and methods for measuring electrical and magnetic properties.
226. Instruments and methods for measurements in radio engineering
227 Instruments and methods for measuring radioactive radiation.

Submitted papers should contain *unpublished original material* in the field of fundamental or applied research It is permitted, however, to send in papers which have previously been published in a technical journal having a limited circulation, but a copy of this publication should be attached to the abstract in this case

Summaries of 150–250 words, presented in at least one of the conference languages (English, French, German or Russian), should be forwarded before 15 November, 1962, to the Member Organisation in Bulgaria, Chinese People's Republic, Czechoslovakia, German Democratic Republic, Hungary, Italy, Japan, Poland, Rumania, Soviet Union, Sweden, United Kingdom and United States of America.

While representatives of technical societies in Austria, Belgium, Denmark, France, German Federal Republic and Yugoslavia also participate in the work of the IMEKO as observers, correspondence from these and other countries not represented by Member Organisations, concerning papers to be presented at the conference, should be directed to the IMEKO Secretariat, Budapest 5, P O. Box 3, Hungary.

SWITZERLAND

Tuesday 27 *August–Saturday* 7 *September* 1963· **Second International Congress of the International Federation of Automatic Control and First International Exhibition of Industrial Electronics.** Basle

Further details of the IFAC Congress may be obtained from the Secretary's Office of the IFAC Congress 1963, Kinkelstrasse 10, Postfach 289, Zurich 35, Switzerland, and of the INEL Electronics Exhibition from the Press Department of Swiss Industries Fair, Postfach, Basle 21, Switzerland.

UNITED KINGDOM

Thursday 25 *October* 1962· **Statistical Approach to Analysis:** Dr. D. A. PANTONY: *Society for Analytical Chemistry, Midlands Section.* Technical College, Nottingham.

Thursday 8 *November* 1962: **Solvent Extraction:** Mr. T. B. PIERCE· *Society for Analytical Chemistry, Midlands Section.* Technical College, Coventry.

Friday 9 *November* 1962. **Some Organic Applications of Polarography:** *Polarographic Society.* College of Advanced Technology, Loughborough.

The collection of spectra—infrared, ultraviolet and other types—to form a central **Spectra Index** from which scientists in this country and abroad will be able to obtain information, has begun at the Scientific Documentation Centre, Dunfermline, Scotland. The Centre was started on a full-time basis one year ago Close liaison is being maintained by the Centre with studies in other parts of the world, especially with U S A., into the particular information retrieval problems found when handling spectra and several publications on the subject have been made by this unit

During the past year, help from industrial and governmental sources has enabled the work to progress, and micro filming, dark-room and workshop facilities have been installed which have made it possible for the collection of spectra to begin.

UNITED STATES OF AMERICA

Thursday–Saturday 1–3 *November* 1962· **Annual Southeastern Regional Meeting of American Chemical Society:** *American Chemical Society, East Tennessee Section* and *Oak Ridge National Laboratory.* Gatlinburg, Tennessee (see *Talanta*, 1962, **9**, 628).

Wednesday–Friday 14–16 *November* 1962 **1962 Eastern Analytical Symposium and Instrument Exhibit:** *Analytical Chemistry Groups of American Chemical Society of New York and North Jersey Sections*, and *New York, Delaware Valley, New England and Baltimore-Washington Sections of Society for Applied Spectroscopy*, and *Metropolitan Microchemical Society.* Statler Hilton Hotel (see *Talanta*, 1962, **9**, 751)

Monday–Thursday 20–23 *May* 1962· **Fourteenth Annual Mid-American Spectroscopy Symposium:** *Society for Applied Spectroscopy, Chicago Section* Sheraton-Chicago Hotel, Chicago.

Original papers are invited from the fields of mass, emission, X-ray, general absorption, infrared, NMR, EPR, Raman and flame spectroscopy, as well as gas chromatography Absolute deadline for receipt to title and abstracts is 15 January, 1963

As in the past, the meeting will feature seminars, problem clinics and an instrument exhibit by leading manufacturers in the fields of spectroscopy and gas chromatography. Further information can be obtained from JOHN E FORRETTE, Roy C Ingersoll Research Center, Borg-Warner Corporation, Wolf and Algonquin Roads, Des Plaines, Illinois, U.S A.

Talanta, 1962, Vol 9, pp 869 to 870 Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Copper^{II} catalysis of 8-acetoxyquinoline hydrolysis: C. R. WASMUTH and HENRY FREISER. (30 *July* 1962)

Sodium peroxide as a flux in refractory and mineral analysis: C B. BELCHER. (30 *July* 1962).

***N,N,N′,N′*-Tetramethyl-o-tolidin (tetron) als reagen zur bestimmung geringer mengen von oxydationsmitteln (Au (III), Ce (IV), BrO_3^- u.a.):** N. JORDANOV and CH. DAIEV. (2 *August* 1962).

A new reductometric reagent—iron^{II} in a strong phosphoric acid medium—II: Titration of molybdenum^{VI} with iron^{II} at room temperature: G. GOPALA RAO and SEETARAMA RAJU SAGI. (2 *August* 1962).

Indirect spectrophotometric determination of the sulphate ion: VLADIMIR PALATY. (2 *August* 1962).

Photometric determination of boron in aqueous medium with phthalein violet: VENCESLAV PATROVSKY. (2 *August* 1962).

Use of $Me^{2+}TiO(C_2O_4)_2.cH_2O$ type compounds in analytical chemistry—I: The determination of potassium in barium titanate: H. AREND and J. NOVAK. (2 *August* 1962).

The determination of thiomalic acid: G. ARAVAMUDAN and C. RAMA RAO (2 *August* 1962)

Polarography of Ce^{IV} in acetate buffer: O. P. AGRWAL and R. C. KAPOOR (6 *August* 1962).

Theory of the indicator transition in chelatometry with special reference to the effect of a second metal: GENKICHI NAKAGAWA and MOTOHARU TANAKA. (6 *August* 1962).

The use of oxycellulose for the collection of traces of metal—I: Qualitative investigations: E SCHULEK, ZS. REMPERT-HORVATH and A LASZTITY (15 *August* 1962).

Thermal neutron-activation analysis of titanium using 5.8-minute titanium-51 and rapid radiochemical separations: CHONG KUK KIM and W. WAYNE MEINKE. (16 *August* 1962).

The determination of boron in zirconium and Zircaloy: EUGENE N. POLLOCK and LAWRENCE P. ZOPATTI. (16 *August* 1962)

The analysis of beryllium and beryllium oxide—VII. The determination of nickel: JAMES O. HIBBITS. (16 *August* 1962)

Cation-exchange separation of bivalent metal ions from rare earths: JAMES S FRITZ and BARBARA B. GARRALDA. (16 *August* 1962).

Determination of sodium in aqueous salt solutions by a glass electrode: JOHN R. GLASS and O. I. MILNER. (16 *August* 1962)

In commemoration of the Hungarian scientist L. W. Winkler, on the centenary of his birth: E. SCHULEK. (14 *August* 1962)

History of Hungarian analytical chemistry: F. SZABADVÁRY. (14 *August* 1962).

Ascorbinometric determination of hypochlorite and hypobromite based on thallium^{III} titration: L. ERDEY and K. VIGH (14 *August* 1962)

Investigations on the accuracy of zinc determinations by atomic absorption methods: L. ERDEY, G. SVEHLA and L. KOLTAI. (14 *August* 1962).

2-Hydroxy-4-amino-4′-methoxydiphenylamine, a new redox indication: L ERDEY, I. KÁSA, T. MEISEL. (14 *August* 1962)

Microdetermination of cyanide ions with radioactive precipitate exchange: E. BÁNYAI, F. SZABADVÁRY and L. ERDEY (14 *August* 1962)

Titration of thallium^{I} ions using chemiluminescent end-point detection: I BUZÁS and L. ERDEY. (14 *August* 1962).

Derivatographic determination of calcite content of bauxites: F. PAULIK, G LIPTAY and S. GÁL. (14 *August* 1962)

Application of the flask method for the analysis of high-halogenated organic substances: L. MÁZOR, K. M. PÁPAY and P KLATSMÁNYI (14 *August* 1962).

The use of a plate electrode for spectrochemical analysis of solutions: T. KÁNTOR. (14 *August* 1962).

The role of rate of atomisation in flame photometry: E PUNGOR and M MAHR. (14 *August* 1962)

Inorganic chromatographic investigations in a glacial acetic acid medium: I KRAUSZ, I. R TAKÁCS and A E. HAVAS (14 *August* 1962).

Titrations in non-aqueous medium with a standard solution of amidazophene (dimethylamino-phenyl pyrazolone)—I: Determination of carboxylic chlorid and their decomposition products: L. BARCZA, (14 *August* 1962).

Analytical control methods for polyvitamin preparations: K. BURGER. (14 *August* 1962).

New methods for the determination of *p*-aminosalicylic acid (PAS): E. SCHULEK, L. MAROS and I MOLNÁR (14 *August* 1962).

Investigation of changes in the oxidation state of cerium in hot sulphuric acid solutions: I PAIS, E SCHULEK and M. RÓZSAHEGYI. (14 *August* 1962)

Determination of *p*-aminobenzoic acid-*N*,*N*-diethyl leucynol ester methane sulphonate and its decomposition with 0,05 *N* tetrabytylammonium methoxide: I GYENES and A LÁSZLÓ. (14 *August* 1962)

A general paper chromatographic method for orientative qualitative analysis: A SCHNEER-ERDEY. (14 *August* 1962).

Untersuchungen über das Kakothelin als Redox-Indicator: P SZARVAS and J LANTOS (14 *August* 1962)

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Photometrische Molybdänbestimmung mit Phenylhydrazin I. Neue Untersuchungen über den Phenylhydrazin-Molybdänkomplex: I. BOZSAI. (14 *August* 1962)

Indikatorsysteme auf Vanadiumkomplexonatis: I. SAJÓ. (14 *August* 1962)

Auf den Schwärzungsunterschieden der Manganlinien beruhende neue qualitative Auswertungsmethode, zur Bestimmung des Mangangehaltes der Aluminiumlegierungen—I: L PÉTER (14 *August* 1962).

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Zerstorungsfreie spektrochemische Analyse archàologischer Bronzefunde: K DOERFFEL and R. WAGNER (21 *August* 1962).

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Precipitation from mixed solvents—III: Magnesium 8-hydroxyquinolate: L C HOWICK, N L FORD and J. L. JONES. (23 *August* 1962).

Precipitation from mixed solvents—IV: Copper 8-hydroxyquinolate: L C HOWICK and J L. JONES (23 *August* 1962)

Liquid scintillation counting of plutonium-239 from biological samples: T Y. TORIBARA, D. A MORKEN and C PREDMORE (24 *August* 1962)

The separation and determination of plutonium in diverse biological samples: T. Y TORIBARA, C. PREDMORE and P. A HARGRAVE (24 *August* 1962)

Contributions to the basic problems of complexometry—XI: The determination of iron and titanium in the presence of aluminium: RUDOLF PŘIBIL and VLADIMÍR VESELÝ (27 *August* 1962).

Sorption of ferroin on silica and its analytical use: FRANTISEK VYDRA and VERA MARKOVÁ. (27 *August* 1962)

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A POLAROGRAPHIC STUDY OF DISSOLVED OXYGEN—PART II*

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Summary—An investigation of the two oxygen reduction waves in aqueous potassium chloride has been made. The first wave is reversible to a considerable degree, the second almost irreversible.

ONE of the most interesting aspects of the study of dissolved oxygen is the degree of reversibility of its reduction at the dropping mercury electrode. Heyrovsky[1] has suggested that the reversibility of this electrode process may be hindered by the unlikelihood of direct capture, by an ion, of two electrons simultaneously; Glasstone[2] has pointed out that non-reversible reactions occur most frequently with non-ionised substances. It has, however, been stated by Breyer[3] that the reduction of oxygen is reversible in alkaline solution.

The second-stage reduction (of hydrogen peroxide) was studied by Chodkowski[4] at pH 13·5–14·2 and was found to be reversible.

A close study of the oxygen–peroxide couple was made by Kern,[5] who found that at pH values above 11 the couple is completely reversible.

Evidence for reversibility may also be obtained from the standard electrode potential of a substance; this has, in fact, been done by Berl[6] who has shown that the electrode reaction at activated carbon electrodes in strongly basic solutions is reversible, being equivalent to an oxygen electrode whose potential corresponds to the reaction:

$$O_2 + H_2O + 2e \rightleftarrows OH^- + HO_2^-.$$

This reaction is also put forward by Hickling[7] who deduces that the discharge of $OH^- \rightarrow OH + e$ is rapid. Kern,[5] however, considers that the HO_2^- ion itself is discharged and that the OH^- ion acts merely as a proton acceptor, while Heyrovsky[8] favours a direct reduction of the oxygen molecule.

In non-basic media Busch and Saywer,[9] Breyer,[3] and others state that both reductions are irreversible. Both Hacobian[10] and Kalousek,[11] however, have concluded that the first reduction of oxygen in unbuffered neutral solutions is reversible. This may be because AC polarographic techniques were employed in these studies, since it has been reported by Glasstone[12] that the oxygen overpotential is reduced by the superimposition of AC, this reduction in effect corresponding to an increase in reversibility. This agrees with the fact that Bowden and Keenan[13] found that in alkaline solutions the oxygen overpotential decreased as the hydroxyl ion concentration increased.

Von Stackelberg[14] and Kolthoff and Miller[15] state that both reductions are irreversible in all media, the latter having studied the reduction of oxygen in various buffers at pH values between 1 and 10.

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The observation by Kolthoff and Miller that the half-wave potentials of both waves are independent of pH leads them to the assumption that the reductions are not reversible, since for the reaction

$$O_2 + 2H^+ + 2e \rightarrow H_2O_2,$$

the equation for the potential E_{de} at each point of the wave is

$$E_{de} = E_{\frac{1}{2}} + \frac{RT}{nF} \ln \left\{ \frac{[O_2][H^+]^2}{[H_2O_2]} \right\}$$

$$= E_{\frac{1}{2}} + \frac{RT}{2F} \ln \left\{ \frac{[O_2]}{[H_2O_2]} \right\} + \frac{RT}{F} \left\{ \ln [H^+] \right\}$$

$$= E_{\frac{1}{2}} + \frac{RT}{2F} \ln \left\{ \frac{[O_2]}{[H_2O_2]} \right\} - \frac{RT}{F} . \text{pH},$$

i.e., that a change in pH of one unit should cause a shift of approximately 60 mV in $E_{\frac{1}{2}}$.

These findings of Kolthoff and Miller[15] are in agreement with those of Kern[5] who found an independence of $E_{\frac{1}{2}}$ with pH for oxygen up to pH 11, where the value of $E_{\frac{1}{2}}$ merges with that of the hydrogen peroxide wave, and the two then follow the theoretical course for a reversible couple.

It was stated, however, by Kolthoff and Miller that as the pH dropped the wave for oxygen became drawn out, giving a more symmetrical wave and a straighter log plot. This, according to Meites,[16] is a good indication of reversibility and implies that some measure of reversibility was in fact attained in the reduction of oxygen at lower pH values.

Since the evidence for the reversibility or otherwise of oxygen reduction in neutral or acid solution seemed uncertain, it was decided to investigate the two reductions.

EXPERIMENTAL

In order that one may apply certain polarographic tests to the reduction waves for this purpose, it is first necessary to establish that the limiting current produced by the reduction is, in fact, primarily diffusion-controlled. Various criteria are available, such as the proportionality of limiting current with concentration of depolariser $I_{lim} = k . C$ which is one simplified form of the

TABLE I

h, *cm*	I, μA 1st reduction	I, μA 2nd reduction	$\frac{I_1}{h^{\frac{1}{2}}}$	$\frac{I_2}{h^{\frac{1}{2}}}$
40	1·85	1·45	0·293	0·229
50	2·0	1·60	0·283	0·226
60	2·2	1·75	0·284	0·226

Ilkovic equation. This equation has already been shown to be followed (in Part I of this work) by each reduction wave and thus a strong indication of a diffusion-controlled process was obtained. Further evidence to support this view is the variation of diffusion current with mercury height. For a diffusion-controlled current it can be shown[17,18] that $I = kh^{\frac{1}{2}}$. As can be seen from the Table I this was so over the range studied.

Since, therefore, the limiting currents produced by the two reductions may be taken as diffusion-controlled, further considerations can be taken into account. It can be shown, for instance,[16,17,18] that for a reversible electrode reaction

$$E_{de} = E_{\frac{1}{2}} - \frac{RT}{nF} \log \frac{I}{I_d - I}$$

where E_{de} = the potential of the polarised electrode,
$E_{\frac{1}{2}}$ = the half-wave potential of the depolariser,
R = the gas constant,
T = the absolute temperature
n = the number of electrons involved in the electrode reaction,
I = the current corresponding to a point on the curve at a potential E_{de},
I_d = the limiting current of the electrode reaction,
and F = the faraday.

This, at 25°, reduces to

$$E_{de} = E_{\frac{1}{2}} - \frac{0{\cdot}0591}{n} \log \frac{I}{I_d - I}.$$

Thus, for a reversible diffusion-controlled current the plot of E_{de} against $\log \frac{I}{I_d - I}$ will be a straight line of slope $\frac{0{\cdot}0591}{n}$ at 25°.

At the point when $I = I_{d/2}$, $\log \frac{I}{I_d - I}$ becomes zero, and the potential is that of the half-wave potential.

Although a reversible wave will thus give a linear log plot the converse is not necessarily true, although it does indicate some degree of reversibility. If the value of n is known, a better criterion is obtained from measurement of the slope of this plot, since departure from the theoretical slope is a good indication of irreversibility.

When obtaining values to be used in a log plot the following factors must be taken into consideration.

Correction of both I and I_d must be made for the charging current in solution, and care must be taken that the resistance of the polarographic cell is not high enough to cause an appreciable error in measurements of potential through the voltage drop across the cell. If the cell resistance is higher than about 1000 Ω, correction must be made for the potential drop across this resistance.

In the polarograms obtained in these studies the potential drop was negligible, since the cell resistance was of the order of 400 Ω. This, at the maximum current of 2 μA, would cause a potential drop of no more than 800 μV (0·8 mV).

If the reaction studied is a slow one at the dropping mercury electrode, the curve obtained will change if the rate of potential application is changed. Runs were therefore carried out using half the usual rate of voltage application to determine whether any obvious difference in the curve occurred. No significant change in wave heights or half-wave potentials was found.

TABLE II.—$E_{\frac{1}{2}}$ AND 'SLOPE' OBTAINED FROM LOG PLOTS FOR OXYGEN IN 0·1*N* KCl.

Dissolved oxygen, *ppm*	$E_{\frac{1}{2}}$ mV		Slope of log plot	
	I_a	I_b	I_a	I_b
7·82	93	893	0·0732	0·221
5·28	106	873	0·0694	0·208
4·62	95	895	0·0728	0·211
4·62	95	892	0·0663	0·218
3·82	104	905	0·0718	0·255
2·81	85	878	0·0855	0·222
1·56	108	911	0·0892	0·240
Average	98	893	0·0740	0·225

A series of log plots were made of values from curves obtained with solutions of oxygen containing from 1·5 to 8 ppm of dissolved oxygen. Nearly all the plots resulted in straight line relations between E and $\log \frac{I}{I_d - I}$ (Fig. 1), only a few giving indications of a plot formed from two intersecting straight lines, which, according to Kern,[5] is a characteristic of irreversible reactions.

The values of the half-wave potentials obtained from these plots were consistent at each oxygen concentration, without any trend to show the dependence of half-wave potential with depolariser concentration; this, according to Meites,[16] is a good indication of an irreversible reaction.

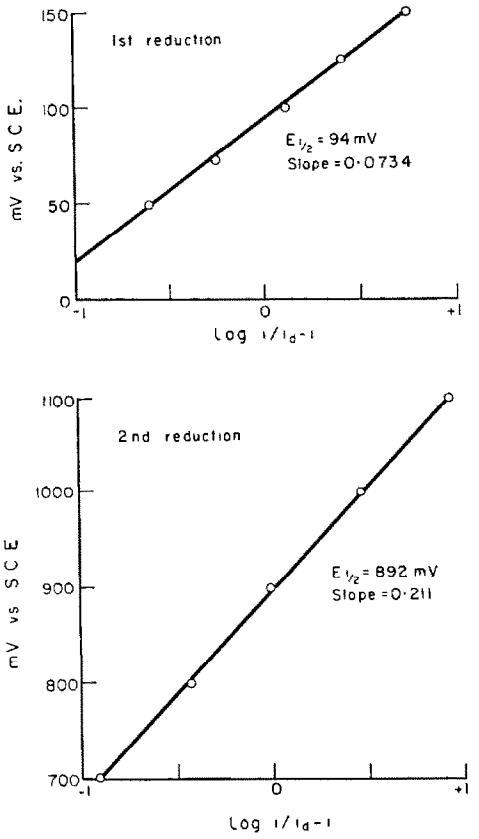


FIG. 1.—Log plots for the reduction of oxygen at a dropping mercury electrode.

The average value for the half-wave potential of the first reduction wave of oxygen in 0·1*N* potassium chloride solution was found to be 98 mV *vs.* the saturated calomel electrode, while that for the second reduction wave was 893 mV *vs.* the saturated calomel electrode. (Approximate values of 94 and 966 mV were also obtained using a cathode-ray polarograph—see later.) These agree reasonably well with the results quoted by other authors for the same, or similar base electrolytes.

In 0·5*N* potassium chloride, for example, Giguere and Lauzier[19] found the half-wave potentials to be 70 mV and 820 mV respectively. Kolthoff and Miller[15] gave 50 and 900 mV for the reductions in 0·01*N* potassium chloride, and Kern[5] gave a value of 65 mV for the half-wave potential of the first reduction wave in 0·05*N* sodium sulphate. Zuman[20] has found values for the second wave of 940 mV and 1010 mV in acid-base solutions and in neutral base solutions, respectively.

An interesting indication of the relative degree of reversibility of the two reductions of oxygen is obtained by a consideration of the slopes of the log plots for each wave.

As indicated earlier, this slope is equal to $0{\cdot}0591/n$ for a reversible reaction at 25°, n being the

number of electrons involved in the reaction. For the reductions considered, carried out at 20°, this becomes $\frac{0{\cdot}0581}{n}$ or 0·0291 for each reduction, since both are two-electron processes.[15]

The average values of the slopes obtained over the range of oxygen concentration were 0·0740 for the first, and 0·225 for the second wave, neither slope showing any dependence on oxygen concentration (see Table I).

From these values it can be seen that the first wave is by no means completely reversible, while the second shows a very large degree of irreversibility. The latter is also borne out by the unsymmetrical shape of the second wave.

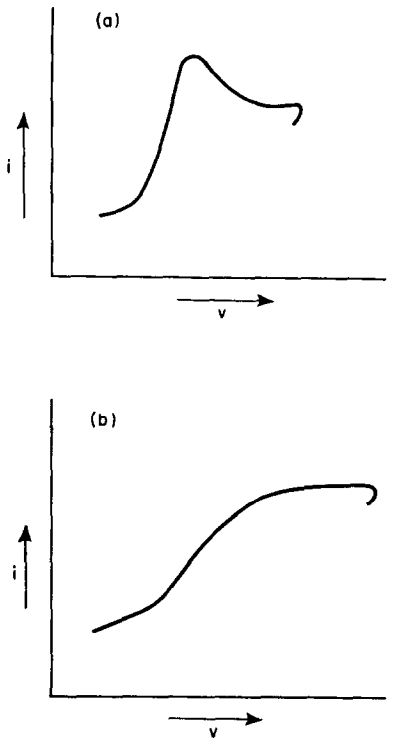


FIG. 2.—Oxygen waves obtained with a cathode-ray polarograph (oxygen in 0·1*N* KCl)

It has been suggested by Taylor and Smith[21] (quoting Kivalo *et al.*[22]), that for an irreversible reaction the value of $E_{\frac{1}{4}}$ obtained depends upon the capillary used. The values obtained using two electrodes were therefore compared, but no significant difference was found.

Valuable evidence agreeing with the fact that the first wave is relatively reversible, while the second is irreversible, was obtained by the use of a cathode-ray polarograph (by kind permission of Southern Instruments Ltd.).

It was found that the first reduction gave the curves shown in Fig. 2a, while the second reduction gave a very flat wave typical of an irreversible reaction (Fig. 2b).

The first wave gave a good linear plot of peak current against oxygen concentration, the current/concentration ratio being considerably greater (1 μA per ppm as against 0·2 μ A per ppm) than that using a normal polarograph, as is to be expected when using this type of instrument. Since the measurements were carried out using a mercury pool anode, the exact potentials were not known. The anodes hould, however, approximate to a 0·1*N* calomel electrode, and thus by taking the potential of the anode as being close to this, the half-wave potentials obtained were of the order of 94 mV for the first and 966 mV for the second wave, thus giving results comparable with those obtained with the DC polarograph.

Since the first reduction of oxygen gave a typical peaked curve, it can be assumed that this reduction does in fact possess a high percentage of reversibility. This fact is further confirmed by the evidence from the "Polaroscope Krizik" (by kind permission of Nash and Thompson Ltd.).

Since the potential sweep employed on this instrument is from 0 to −2 V, both reduction waves should show their presence. A typical curve obtained is given in Fig. 3.

The presence of a reversible reaction is shown by a dip or notch in the curve; this is given by the first stage reduction but is rather indefinite for the second. Moreover, if the reaction is wholly reversible a matching notch should appear on the lower wave as the potential returns from −2 to 0 volts.

No secondary notch is seen for the second wave, but one is apparent, though a little displaced, for the first. This shows that the first reaction, while not wholly reversible, is appreciably so, while the second is almost completely irreversible.

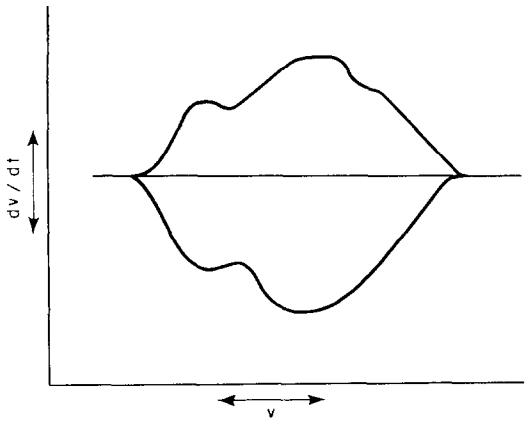


FIG. 3.—Curve obtained for oxygen reduction using the "Polaroscope Krizik".

CONCLUSIONS

Virtually all the tests show the high degree of irreversibility of the second reduction. The first reduction shows a certain degree of non-reversible character, as exemplified by the non-theoretical slope of its log plot, by the non-dependence of half-wave potential with pH, by indications from the cathode-ray polarograph that the half-wave potential alters slightly with oxygen concentration (although no sign of this was shown by the conventional DC polarograph) by the slightly unsymmetrical nature of the "Polaroscope Krizik" curve, and also by the fact that the curve obtained normally with the DC polarograph using an applied potential increasing negatively is not exactly reproduced if the direction of potential increase is reversed. Conversely, indications of a considerable degree of reversibility of the first wave are shown by the fact that a good peaked curve is shown by the cathode-ray polarograph, the peak height being proportional to oxygen concentration (at least over a range of 1 to 10 ppm). This is supported by the occurrence of a notch in the "Polaroscope" $\frac{dv}{dt}\Big/V$ curve and of its corresponding notch when the direction of applied potential is reversed. Further evidence, though of a rather negative kind, is given by the lack of change in half-wave potential with the capillary used, and of the lack of effect of concentration either upon log plot slope or on the half-wave potential obtained from the plot.

Thus it would appear that the first reduction of oxygen dissolved in a 0·1*N* aqueous solution of potassium chloride is reversible to a considerable degree but that the second reduction may be considered as virtually irreversible.

Zusammenfassung—Eine Untersuchung der zwei polarographischen Reduktionswellen von Sauerstoff in wässriger Losung wurde durchgefuhrt. Die erste Welle ist zu beträchtlichem Masse reversibel, die zweite nahezu volkommen irreversibel.

Résumé—Les auteurs ont étudié les deux vagues de réduction de l'oxygene en milieu chlorure de potassium. La première vague est réversible, la seconde presque irréversible.

REFERENCES

[1] J. Heyrovsky, *Farad. Soc. Discussions*, 1947, **1**, 220.
[2] S. Glasstone, *Textbook of Physical Chemistry*. Macmillan and Co. Ltd., 2nd Ed., 1948.
[3] B. Breyer, *Malayan Pharmaceutical Journal*, 1956, **5**, 116.
[4] J. Chodkowski, *Roczniki Chem.*, 1953, **27**, 309, *Chem. Abs.*, 1954, **48**, 13468_i.
[5] D. M. H. Kern, *J. Amer. Chem. Soc.*, 1954, **76**, 4208.
[6] W. Berl, *J. Electrochem. Soc.*, 1943, **83**, 253.
[7] A. Hickling, *Quart. Revs.*, 1949, **3**, 95.
[8] J. Heyrovsky, *Polarographie*. Springer-Verlag.
[9] A. W. Busch and C. N. Saywer, *U.S. Atomic Energy Commission* NYO 4436.
[10] S. Hacobian, *Austral. J. Chem.*, 1953, **6**, 211.
[11] M. Kalousek, *Coll. Czech. Chem. Comm.*, 1948, **13**, 105.
[12] S. Glasstone, *J. Amer. Chem. Soc.*, 1925, **47**, 940.
[13] F. P. Bowden and H. W. Keenan, quoted in F. P. Bowden and J. N. Agar, *Ann. Reports*, 1938, **35**, 90.
[14] M. v. Stackelberg, *Polarogarphische Arbeits-Methoden*. Walter de Gruyter and Co., Berlin, p. 320.
[15] I. M. Kolthoff and C. S. Miller, *J. Amer. Chem. Soc.*, 1941, **63**, 1013.
[16] L. Meites, *Polarographic Techniques*. Interscience, N.Y., 1955.
[17] I. M. Kolthoff and J. J. Lingane, *Polarography*. Interscience, N.Y., 2nd Ed., 1952.
[18] G. W. C. Milner, *Polarography*. Longmans, Green and Co., London, 1957.
[19] P. A. Giguere and L. Lauzier, *Canad. J. Res.*, 1945, **23, B76**, 223.
[20] P. Zuman, *Coll. Czech. Chem. Comm.*, 1950, **15**, 1113.
[21] J. K. Taylor and S. W. Smith, *J. Res. Nat. Bur. Stand.*, 1956, **56**, 143.
[22] P. Kivalo, K. B. Oldham and H. A. Laitinen, *J. Amer. Chem. Soc.*, 1953, **75**, 4148.

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THE DETERMINATION OF TRACES OF ARSENIC AND ANTIMONY IN SAMPLES OF PLATINUM BY NEUTRON-ACTIVATION ANALYSIS

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Summary—A method is described for the determination of ultramicro quantities of arsenic and antimony in pure platinum. In order to avoid self-shielding differences between samples and standards during neutron irradiation, comparators have been prepared by the addition of very small known amounts of arsenic and antimony to analytical samples. The nuclear reactor BEPO at Harwell has been used as the neutron source; 0·1-g samples of platinum have been taken for the determinations, and a radiochemical separation procedure using carriers has been employed to isolate the induced arsenic and antimony activities.

Results of analyses of seven samples of platinum are quoted. Although contents of as little as 10^{-8} g of either arsenic or antimony were determined, the ultimate sensitivity of the method was not approached.

IN connection with an investigation of the effects of impurities on the electrical and mechanical properties of precious metals, it proved desirable to develop a new neutron-activation method for the determination of traces of arsenic and antimony present in samples of purified platinum.

The nuclear characteristics of arsenic and antimony relevant to activation with thermal neutrons are summarised in Table I. The fact that the half-lives of ^{76}As, ^{122}Sb and ^{124}Sb are 26·6 hr, 2·80 d, and 60·4 d, respectively, made it possible to devise an analysis procedure involving radiochemical separation of first arsenic and then antimony. Because of their short half-lives, 3·5 min ^{122m}Sb, 1·3 min ^{124m}Sb, or 21 min ^{124m}Sb could not be used in the determination of antimony.

It has been estimated[1] that with a thermal neutron flux of 10^{12} neutrons/cm^2/sec, it should be possible under ideal conditions to determine *ca.* 5×10^{-11} g of arsenic, utilising the activated form ^{76}As. The corresponding calculated sensitivity for antimony is 1×10^{-10} g, using ^{122}Sb with ^{124}Sb.

Possible conflicting nuclear processes which may limit the neutron-activation analysis of arsenic and antimony are listed by Koch.[2] However, these do not give rise to interference in the present case.

In order to avoid errors from self-shielding, standardisation has been provided by irradiating similar known quantities *a* and *b* of a sample with very small known amounts of arsenic and antimony mixed with *b*.

EXPERIMENTAL

Irradiation

About 0·1-g samples of platinum, in the form of powdered sponge, were accurately weighed and sealed in silica irradiation tubes of 4-mm internal diameter. Standardisation was provided by the

TABLE I.—NUCLEAR DATA FOR THERMAL NEUTRON ACTIVATION OF ARSENIC AND ANTIMONY.

Target nuclide	Abundance %	Isotopic activation cross section, *barns*	Product on thermal neutron irradiation	Radiation and energy, *MeV*	Half-life
^{75}As	100	5·4 ± 1·0	^{76}As	β^- 2·97 (50%), 2·41 (31%), 1·76 (15%), 0·36 (3%); γ 0·560, 0·64, 1·20, 1·40, 2·05	26·6 hr
^{121}Sb	57·25		^{122m}Sb	IT γ 0·061, 0·075	3·5 min
		6·8 ± 1·5	^{122}Sb	β^+ (0·01%) 0·565; β^-(97%) 0·74, 0·90, 1·40, 1·97; EC (3%); γ 0·566, 0·686, 1·137, 1·256.	2·80 d
^{123}Sb	42·75	0·03 ± 0·015	^{124m}Sb	IT γ 0·012; β^- 3·2.	1·3 min
		0·03 ± 0·015	^{124m}Sb	IT γ 0·0185; β^- (W) ~ 2·5.	21 min
		2·5 ± 0·5	^{124}Sb	β^- 0·202, 0·36, 0·608, 0·745, 0·871, 0·930, 1·590, 1·658; γ 0·603, 0·632, 0·645, 0·713, 0·722, 0·967, 1·05, 1·33, 1·37, 1·45, 1·70, 2·09, 2·3	60·4 d

addition of weighed portions (*ca.* 0·05 g) of standard solutions of arsenic (20 mg of As/litre, as As^{III} in 2·5*M* HCl) and antimony (20 mg of Sb/litre, as Sb^{III} in 2·5*M* HCl) to 0·1-g samples of platinum in silica irradiation tubes. The liquids were allowed to soak into the metal powder, which was then carefully dried at 70°, after which the tubes were sealed.

Comparators containing the added arsenic and antimony, together with samples to which no arsenic and antimony had been added, were packed with silica wool in standard aluminium screw-top cans and sent to the Atomic Energy Research Establishment, Harwell, for activation. Irradiations were for 1 week in the nuclear reactor BEPO, at Pile Factor 10–12.

Radiochemical separation

Following delivery from Harwell after irradiation, the samples were put through a radiochemical procedure to separate arsenic and antimony radionuclides from interfering activities. Many radiochemical procedures for arsenic and antimony have been described,[3,4] but it was decided to develop a new separation scheme based largely on known solvent extraction behaviour,[5–10] as it was felt that this could be more rapid and convenient than methods involving distillation steps. Ten milligrams of inactive arsenic and 10 mg of inactive antimony were added as carriers, and the radiochemically pure elements obtained from the chemical separations were precipitated for counting as metal and trisulphide,[11] respectively. The chemical yields were determined gravimetrically and were usually about 50% for arsenic and 70% for antimony.

Preliminary experiments with ^{76}As and ^{121}Sb tracers showed that there were no losses of arsenic or antimony by volatilisation accompanying the dissolution of samples.

Preparation of carriers

Arsenic: (10 mg of As/ml). Dissolve 3·30 g of AnalaR As_2O_3 in 20 ml of 2*M* NaOH. Dilute the solution to 100 ml, make it just acid by the addition of 1*M* HCl and transfer it to a 250-ml calibrated flask. Add 2 g of $NaHCO_3$ and when this has dissolved dilute to volume with H_2O.

Antimony: (10 mg of Sb/ml). Dissolve 6·67 g of Analar $KSbC_4H_4O_7$ in H_2O and dilute to 250 ml in a calibrated flask.

The carriers may be conveniently standardised periodically by titrating 5- or 10-ml aliquots with 0·1*N* $KBrO_3$, using *p*-ethoxychrysoidine as a reversible indicator.

Radiochemical separation procedure

Treat each sample in the following manner:

Step 1: Remove a silica irradiation tube from the can, open it at the construction and transfer the contents quantitatively to a 150-ml beaker containing 1 ml of standard As-carrier, 1 ml of standard Sb-carrier, and 5 ml of 12*M* HCl. Wash out the tube thoroughly with warm 6*M* HCl and transfer the washings to the beaker. Heat on a water-bath and add the minimum quantity of 16*M* HNO_3 necessary to dissolve the platinum. Remove HNO_3 by heating with three portions of hydrochloric acid-hydrogen peroxide solution (2 ml of 12*M* HCl and 1 ml of 30% H_2O_2). Add 2 mg of Au (as Au^{III} in 0·1*M* HCl) and evaporate to a volume of 5 ml, with the addition of small amounts of H_2O_2 from time to time. Transfer the solution to a clean 50-ml centrifuge tube.

Step 2: Dilute the solution to 15 ml with H_2O, warm to 80° and add 10 ml of 10% NH_4Cl dropwise with stirring. Cool in ice for 15 min to ensure essentially complete precipitation of $(NH_4)_2PtCl_6$. Centrifuge and transfer the supernate to a clean 50-ml centrifuge tube. To the solution add 0·5 g of $N_2H_4 \cdot 2HCl$ and digest on a water-bath for 10 min to precipitate Au. Centrifuge, and transfer the supernate to a 100-ml separating funnel.

Step 3: To the solution add 10 ml of 12*M* HCl, 10 ml of 18*M* H_2SO_4 and 2 drops of 10% KI solution. Cool and extract As^{III} by agitating with three 10-ml portions of $CHCl_3$. Separate and combine the organic extracts for *arsenic determination* and retain the aqueous phase for *antimony determination.*

Step 4. *Procedure for arsenic:* Wash the organic phase with two 10-ml portions of 6*M* HCl and discard the washings. Transfer the organic layer to a clean 50-ml centrifuge tube. Add 10 ml of 1% $N_2H_4.2HCl$ solution and agitate to extract arsenic into the aqueous layer. Separate the aqueous layer into a clean centrifuge tube and discard the organic phase. To the aqueous solution add 20 ml of 12*M* HCl and 5 ml of 20% $(NH_4)H_2PO_2$. Digest until the precipitate of As coagulates. Centrifuge and discard the supernate. Wash the precipitate with two 10-ml portions of H_2O.

Step 5: Add a few drops of Sb carrier solution and a few drops of Ge carrier (10 mg of Ge/ml as Ge^{IV} in 2*M* NaOH). Digest with 5 ml of 12*M* HCl and 2 ml of 30% H_2O_2 to dissolve the As. Add 10 ml of 6*M* HCl, cool, and extract Sb^V with two 10-ml portions of (*iso* $C_3H_7)_2O$. Separate and discard the organic phases. Make the aqueous phase at least 9*M* in HCl and extract Ge^{IV} with two 10-ml portions of CCl_4. Discard the organic phases.

Step 6: To the aqueous solution add 5 ml of 20% $(NH_4)H_2PO_2$. Digest on a water bath until the precipitate of As coagulates. Centrifuge and wash the precipitate with three 10-ml portions of H_2O. Finally transfer the As with a little H_2O to a weighed aluminium counting tray, evaporate to dryness under an infrared lamp and determine the chemical yield.

Step 7: *Procedure for antimony:* To the aqueous solution from Step 3 add 2 ml of 0·1*N* $Ce(SO_4)_2$ to oxidise Sb^{III} to Sb^V. Extract Sb^V with three 10-ml portions of (*iso* $C_3H_7)_2O$. Separate and combine the organic phases. Wash the combined organic extract with 10 ml of 6*M* HCl and discard the washings. Add 5 drops of 12*M* HCl and evaporate off the solvent. To the residue add 3 ml of 18*M* H_2SO_4 and 1 ml of 1% $N_2H_4.2HCl$, and dilute to 20 ml with H_2O. Add 1 ml of 10% KI and extract Sb^{III} with two 10-ml portions of C_6H_6. Separate and combine the organic layers.

Step 8: Back-extract Sb^{III} from the organic phase by agitating with 10 ml of 6*M* NaOH. Separate the aqueous layer into a clean 50-ml centrifuge tube and dilute to 20 ml with warm H_2O. Add 1 g of $Na_2S_2O_4$ and digest on a water-bath for 10 min. Centrifuge and discard the supernate. Wash the precipitate of Sb with H_2O.

Step 9: Dissolve the Sb in the minimum quantity of 12*M* HCl and 30% H_2O_2. Adjust the acidity of the solution with NaOH until it is only just acid and there is no turbidity. Add 25 ml of a saturated solution of NH_4CNS and digest on a water-bath until the precipitate of Sb_2S_3 coagulates. Centrifuge, and wash the precipitate thoroughly with H_2O before transferring it to a weighed aluminium counting tray. Evaporate to dryness under an infrared lamp and determine the chemical yield.

Measurement of radioactivity

The separated samples of arsenic and of antimony trisulphide were counted under a thin end-window Geiger-Müller counter (EHM 2/S), with associated electronic equipment. All measured

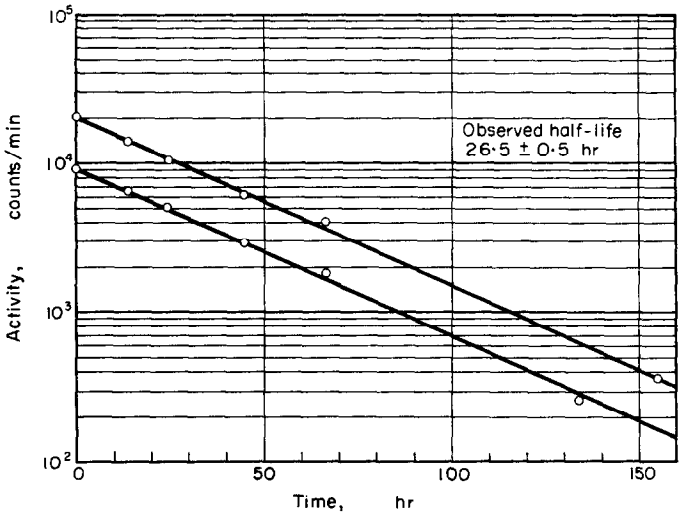


FIG. 1.—Typical decay curves from final precipitates of arsenic.

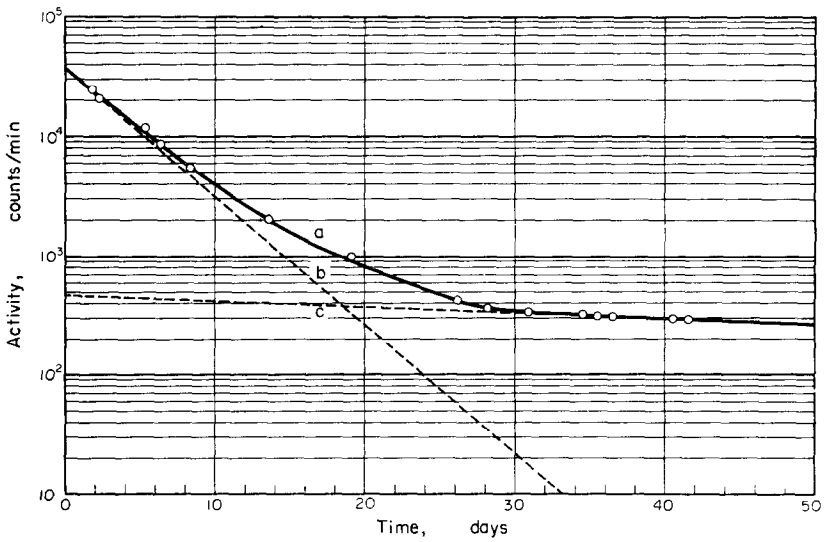


FIG 2.—Part of a composite decay curve from a final precipitate of antimony trisulphide:
(a) Composite decay curve.
(b) Antimony—122 activity (observed half-life, 2·8 ± 0·1 d.)
(c) Antimony—124 activity (observed half-life, 61 ± 2 d.)

activities were corrected for paralysis, background, and chemical yield, and for any decay of significance between measurements on precipitates from samples and comparators. Since the maximum β^--energy of ^{76}As is 2·97 MeV no correction for self-absorption was necessary, and similarly for ^{122}Sb with a maximum β^--energy of 1·97 MeV.

Radiochemical purity of the sources was confirmed by plotting decay curves; typical curves are shown in Figs. 1 and 2.

RESULTS

In Table II are shown results of analyses of purified samples of platinum. The method described in this paper has been applied to samples containing as little as 10^{-8}g

TABLE II.—ARSENIC AND ANTIMONY CONTENTS OF SAMPLES OF PLATINUM DETERMINED BY NEUTRON-ACTIVATION ANALYSIS.

Sample	Arsenic found, *ppm*	Antimony found, *ppm*
Pt 1	2·75	5·18
	2·99	5·36
Pt 2	2·94	1·19
	2·77	1·26
Pt 3	4·70	0·95
	5·29	1·01
	4·47	0·93
	4·36	0·86
Pt 4	1·18	4·02
	1·15	4·05
Pt 5	0·106	4·03
	0·104	4·02
Pt 6	0·56	0·14
	0·57	0·14
	0·55	0·14
	0·56	0·14
Pt 7	0·71	3·38
	0·76	3·62

of either arsenic or antimony, but even in these cases the ultimate sensitivity of the method was not approached.

Acknowledgment—We are grateful to The International Nickel Co. (Mond) Ltd., for supplying samples of platinum, for financial support, and for a Research Fellowship to one of us (R. A. K.).

Zussammenfassung—Eine Methode zur Bestimmung von Ultra mikromengen von Arsen und Antimon in reinem Platin wird beschrieben. Um Unterschiede in der Selbstabschirmung zwischen Probe und Standard während der Neutronenbestrahlung zu vermeiden, wurden Vergleichsproben bereitet durch Zugabe sehr kleiner aber bekannter Mengen von Arsen und Antimon zu den Analysenproben. Der Harwellreaktor BEPO wurde als Neutronenquelle verwendet. 0.1 g Proben von Platin wurden herangezogen und radiochemische Methoden unter Anwendung von Trägern wurden benutzt, um die induzierten Aktivitäten zu isolieren. Sieben Resultate werden mitgeteilt. Bis herunter zu 10^{-8} g Arsen oder Antimon wurden bestimmt, was aber noch keineswegs die äusserste Empfindlichkeit der Method ist.

Résumé—Les auteurs décrivent une méthode de dosage d'ultramicroquantités d'arsenic et d'antimoine dans le platine pur. Afin d'éviter des différences d'autoprotection entrê les échantillons et les étalons pendant l'irradiation par les neutrons, des comparateurs ont été préparés par addition de très faibles quantités connues d'arsenic et d'antimoine aux échantillons analytiques. Le réacteur nucléaire BEPO de Harwell a été utilisé comme source de neutrons. Les dosages ont été réalisés sur 0,1 g d'échantillons de platine; une méthode de séparation radiochimique utilisant des entraineurs a été utilisée pour isoler les activités induites de l'arsenic et de l'antimoine.

Les résultats d'analyses de sept échantillons de platine sont donnés. Bien que des teneurs aussi faibles que 10^{-8} g. d'arsenic ou d'antimoine aient été déterminées, la sensibilité la plus grande de la méthode n'a pas été atteinte.

REFERENCES

[1] E. N. Jenkins and A. A. Smales, *Quart. Revs.*, 1956, **10,** 83.
[2] R. C. Koch, *Activation Analysis Handbook*, Academic Press, New York and London, 1960.
[3] H. C. Beard, *The Radiochemistry of Arsenic.* U.S. Atomic Energy Commission Monograph, NAS–NS 3002, 1960.
[4] W. J. Maeck, *The Radiochemistry of Antimony.* U.S. Atomic Energy Commission Monograph, NAS–NS 3033, 1961.
[5] E. B. Sandell, *Colorimetric Determination of Traces of Metals.* Interscience Publishers, New York and London, 3rd Ed., 1959, pp. 280, 256, 50.
[6] W. Fischer and W. Harre. *Angew. Chem.*, 1954, **66,** 165.
[7] F. C. Edwards and A. F. Voigt, *Analyt. Chem.*, 1949, **21,** 1204.
[8] R. W. Ramette, *ibid.*, 1958, **30,** 1158.
[9] K. Tanaka, *Japan Analyst*, 1960, **9,** 573.
[10] H. C. Beard and L. A. Lyerly, *Analyt. Chem.*, 1961, **33,** 1781.
[11] A. A. Smales, D. Mapper, A. J. Wood and L. Salmon, U.K.A.E.A., Atomic Energy Research Establishment, Harwell, Rept. AERE C/R 2254, 1957.

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THE ULTRAVIOLET SPECTRA OF CHLORINE AND ITS OXIDES IN CARBON TETRACHLORIDE

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Summary—Chlorine and its oxides (Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7) give ultraviolet absorption spectra in carbon tetrachloride. These spectra can be used for the determination of the compounds.

INTRODUCTION

IN connection with a study of the radiolysis of carbon tetrachloride[1] a method was required for the rapid determination of chlorine and chlorine oxides directly in this liquid. None of the methods described so far could be adopted.

Many years ago it was found that gaseous chlorine and its oxides show some absorption spectra in the visible light range.[2] Anbar and Dostrevsky[3] measured the ultraviolet absorption spectra of organic hypohalites in carbon tetrachloride. The spectra of some chlorine oxides in water were also published. Chlorine and chlorine oxides are very soluble in carbon tetrachloride and we have examined the ultraviolet spectra of the solutions and the use of these spectra for determination of the substances.

EXPERIMENTAL

Apparatus

A Zeiss universal spectrophotometer, equipped with a hydrogen lamp BGW and NaCl prism were used for the spectrophotometric measurement, with 1-cm cells at room temperature.

Reagents

Carbon tetrachloride: Lachema n.p. carbon tetrachloride, reagent grade, was saturated with chlorine, washed successively with aqueous sodium hydroxide and water, dried over calcium chloride and distilled. The infrared spectrum showed it to be pure and sufficiently dry.

All other chemicals were reagent grade.

RESULTS

I. *Qualitative comparison of spectra*

Chlorine, Cl_2*:* The spectrophotometric determination of chlorine in carbon tetrachloride can be carried out in the ultraviolet region, as was reported a few years ago.[4] Pure gaseous chlorine was prepared by the decomposition of manganese dioxide with hydrochloric acid; it was dried and purified as usual, and dissolved in carbon tetrachloride. In the range 250–450 mμ chlorine shows a simple absorption curve with a maximum at 320 mμ (Fig. 1.).

Chlorine monoxide, Cl_2O*:* The gas was prepared by leading chlorine over mercury oxide at a temperature of 0°. From the reagent tube it was passed directly into the carbon tetrachloride, so that it was accompanied by chlorine. Fig. 2, Curve 1, shows the spectrum of the mixture; the first maximum belongs to chlorine and two other maxima belong to chlorine monoxide. The higher peak is at 395 mμ and the lower at 415 mμ.

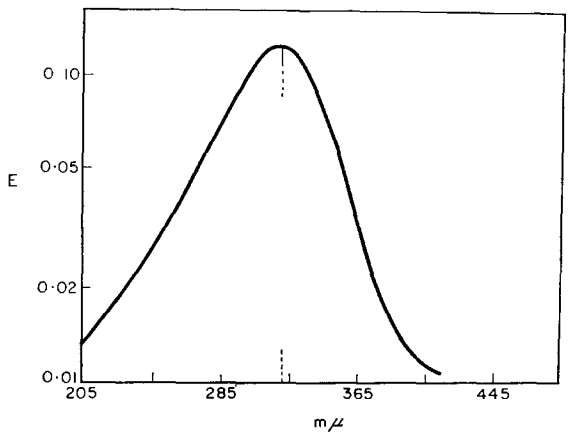


FIG. 1.—Absorption spectrum of chlorine dissolved in carbon tetrachloride.

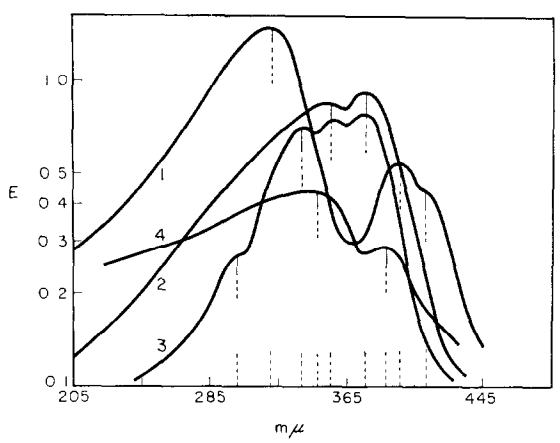


FIG. 2.—Absorption spectra of chlorine oxides dissolved in carbon tetrachloride.
1: $Cl_2 + Cl_2O$; 2: ClO_2; 3: $ClO_2 + Cl_2O_6$; 4: Cl_2O_7.

Chlorine dioxide, ClO_2: The pure compound was prepared by the decomposition of potassium perchlorate with sulphuric acid (in the presence of oxalic acid). Fig. 2, Curve 2, shows the absorption curve, with two maxima, the higher peak at 375 mμ, and the lower at 355 mμ.

Chlorine hexoxide Cl_2O_6: This oxide was prepared by the ultraviolet irradiation of a mixture of chlorine dioxide and oxygen at temperature of 4°. In the vapour form it was bubbled through carbon tetrachloride, and was therefore in solution together with chlorine dioxide. Fig. 2, Curve 3, shows two maxima of chlorine hexoxide. The higher peak is at 340 mμ and the lower at 305 mμ. The other two maxima belong to chlorine dioxide.

Chlorine heptoxide, Cl_2O_7: This was prepared by dehydration of perchloric acid with phosphorus pentoxide, followed by vacuum distillation. Its spectrum is not very characteristic, but this also has two maxima, with wavelengths of 350 mμ for the higher peak and 385 mμ for the lower (Fig. 2, Curve 4).

The wavelengths of the peaks differ so greatly that they can serve as a qualitative

criterion, and it is also possible to determine several oxides simultaneously. The dependence of wavelength on the content of oxygen of the oxides may be noted: the wavelengths of the maxima decrease with increasing oxygen-content (with the exception of chlorine heptoxide), as can be seen from Table I.

TABLE I.—WAVELENGTHS OF MAXIMA OF DIFFERENT CHLORINE COMPOUNDS DISSOLVED IN CARBON TETRACHLORIDE

Solute	higher λ_{max}, $m\mu$	lower λ_{max}, $m\mu$
Cl_2O	395	415
ClO_2	375	355
Cl_2O_6	340	305
Cl_2O_7	350	385
Cl_2	320	—

II. *Quantitative determination*

Pure chlorine was dissolved in carbon tetrachloride and its concentration was determined titrimetrically; the solution of chlorine in carbon tetrachloride was shaken vigorously with aqueous ammonia, the aqueous phase was separated, the excess of ammonia was removed by boiling, and the chloride ion content so formed was determined by titration with silver nitrate:

$$3Cl_2 + 6NH_4OH + 2NH_3 = 6NH_4Cl + 6H_2O + N_2 \qquad (1)$$

Other standard solutions were made by appropriate dilutions of this solutions. The extinction was measured at 320 mμ. Fig. 3 shows the calibration curve. It can be seen that the lower limit of determination is about $2 \times 10^{-5}M$, or 1 μg.

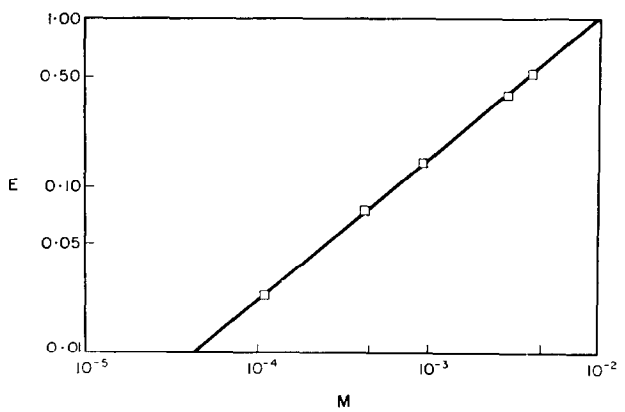


FIG. 3.—Calibration curve for chlorine in carbon tetrachloride at 320 mμ.

For the determination of chlorine monoxide and chlorine dioxide use is made of the effect discovered by Bowen,[2] that both oxides, in carbon tetrachloride, are decomposed by daylight into chlorine and oxygen:

$$2Cl_2O \rightarrow 2Cl_2 + O_2 \qquad (2)$$

$$2ClO_2 \rightarrow Cl_2 + 2O_2 \qquad (3)$$

Through this photolysis the character of the spectra is changed, from those of the oxides to that of chlorine. The determination of chlorine monoxide and dioxide are thus simplified to the determination of chlorine, and the calibration curve for chlorine and the same lower limit apply. The photolysis is complete after about 24 hr, and after that period the chlorine spectra is unchanged. The change in spectrum of chlorine dioxide, for instance, over 24 hr is shown in Fig. 4, after which it was constant.

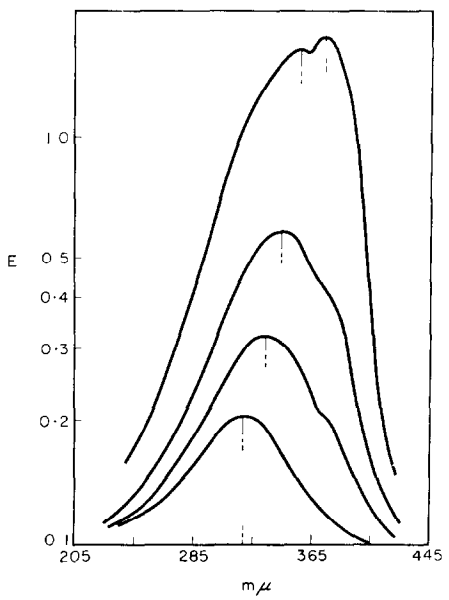


FIG. 4.—Photolysis of chlorine dioxide in carbon tetrachloride.
From top to bottom: fresh solution, 1 hr in daylight;
19 hr in daylight; 24 hr in daylight.

From equation (3) the amount of dioxide originally present can be calculated; for chlorine monoxide the procedure is the same. In the presence of chlorine the concentrations are measured before and after photolysis.

Chlorine hexoxide and heptoxide cannot be determined in the same way, since they are not found to be photolysed in carbon tetrachloride. Standard solutions are prepared and measured as for chlorine using the higher peak. The lower limit for their determination was not established.

CONCLUSION

The ultraviolet spectra of chlorine and its oxides, dissolved in carbon tetrachloride, depend on the chemical constitution, are closely related, and can be used for the determination of chlorine, chlorine monoxide, chlorine dioxide, chlorine hexoxide and chlorine heptoxide. Chlorine monoxide and dioxide can be determined as chlorine after their photolysis; chlorine hexoxide, chlorine heptoxide, and chlorine itself, when dissolved in carbon tetrachloride, are not affected by light.

Acknowledgment—Thanks are due to Mrs. J. Šulcová for her technical help.

Zusammenfassung—Es wurde gefunden dass Chlor und seine Oxyde (Cl_2O, ClO_2, Cl_2O_6 und Cl_2O_7) in Tetrachlorkohlenstoff. Absorptionsspektren im Ultraviolett geben, was zur Analyse der Verbindungen herangezogen werden kann.

Résumé—L'auteur a trouvé que le chlore et ses oxydes (Cl_2O, ClO_2, Cl_2O_6 et Cl_2O_7) donnent des spectres d'absorption ultra-violets dans le tétrachlorure de carbone. Ces spectres peuvent être utilisés pour le dosage de ces composés.

REFERENCES

[1] Z. Spurný, *Coll. Czech. Chem. Comm.*, 1960, **25**, 1254.
[2] A. Bowen, *J. Chem. Soc.*, 1923, **123**, 1203.
[3] M. Anbar and I. Dostrevsky, *ibid.*, 1954, 1105.
[4] Z. Spurný, *Nature*, 1959, **183**, 1390.

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THE INFLUENCE OF THE NATURE OF THE ORGANIC SOLVENT ON THE EXTRACTION OF CHELATE COMPOUNDS

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Summary—The influence of the nature of the organic solvent on the extraction of the thenoyltrifluoroacetonates of Np^{V}, Co^{II} and Ce^{III}, the hydroxyquinolates of Np^{V} and W^{VI}, the acetylacetonates of Co^{II} and Fe^{III}, the 1-nitroso-2-naphtholate of Co^{II}, and some other chelate compounds has been studied. As a rule, "co-ordination-unsaturated" chelates (co-ordination number of the central atom greater than twice its charge, bidentate reagent) are extracted better by ketones, esters, and, particularly, by alcohols; and, normally, are less well extracted by ethers and by hydrocarbons and their halogen-substituted derivatives. The extraction of "co-ordination-unsaturated" chelates can in some cases be favoured by the use of an excess of the reagent. "Co-ordination-saturated" chelate compounds (co-ordination number not greater than twice the charge, bidentate reagent) can be extracted by solvents of extremely diverse nature, including non-oxygen-containing solvents of relatively low polarity. Attention is drawn to the possibility of separating "co-ordination-saturated" and "co-ordination-unsaturated" chelate compounds.

FOR the extraction of the chelate compounds formed by a given reagent with various elements, those solvents are used, as a rule, in which the reagent itself is readily soluble. It is known, for example, that hydroxyquinolates and nitrosonaphtholates are extracted chiefly by chloroform, thenoyltrifluoroacetonates by benzene, dithizonates by carbon tetrachloride or chloroform, and so on. Nevertheless, consideration of only the solubility of a reagent in the organic solvent is insufficient for an understanding of the influence of the nature of the solvent on the extraction of the chelates. There are some data which indicate that the properties of the metal also play an essential role in this.[1–5]

In this paper, the question of the influence of the solvent is considered from the point of view of the co-ordination saturation or unsaturation of the central atom of the chelate compound.

EXPERIMENTAL

Radioactive isotopes with a carrier were used (except for ^{239}Np, which was used without a carrier). The equilibrium concentrations of the elements in the aqueous and organic phases were measured by conventional radiometric methods. Buffer solutions were used to establish the pH; the equilibrium pH was measured by means of a glass electrode. In the majority of cases, the organic reagent was added in the form of a solution in the solvent. The volumes of the organic and aqueous phases were equal (10 ml each) and shaking was carried out in graduated separating funnels for 7 min. Measurements of the volumes of the phases were taken into consideration in calculating the percentage extraction.

RESULTS

The influence of solvents belonging to various classes of organic compounds was investigated. For each solvent, the dependence of the percentage extraction E on the pH of the equilibrium aqueous phase was studied. In all cases, the results of a single extraction are given below.

Chelate compounds of cobalt

The influence of the nature of the solvent on the extraction of the thenoyltrifluoroacetonate and the acetylacetonate of cobalt was studied. Majumdar and De noted that cobalt^{II} was extracted poorly by a benzene solution of thenoyltrifluoroacetone

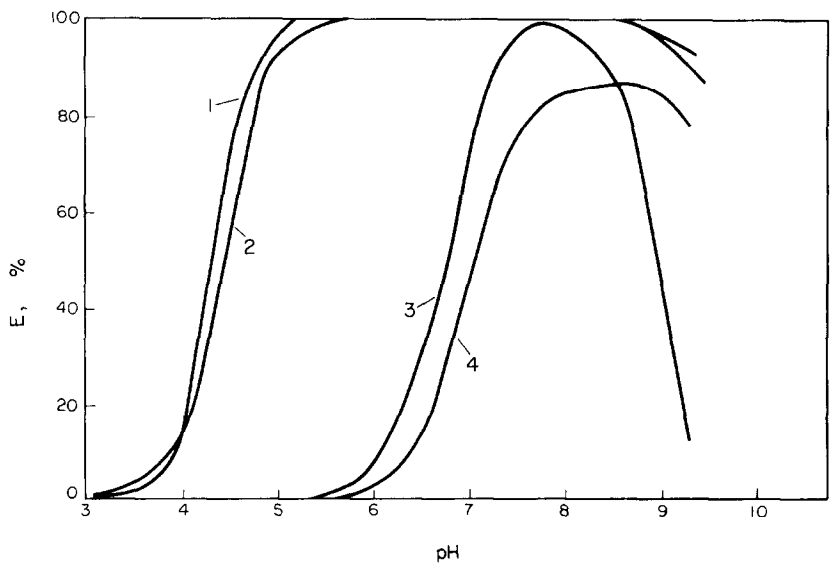


FIG. 1.—Extraction of cobalt^{II} thenoyltrifluoroacetonate:
1—methyl ethyl ketone; 2—n-butanol; 3—benzene; 4—chloroform.

(TTA)[6]. We studied the extraction of cobalt^{II} ($6{\cdot}8 \times 10^{-6}M$) with a $0{\cdot}01M$ solution of TTA in n-butanol, methyl ethyl ketone, benzene, and chloroform. The results obtained are given in Fig. 1. Benzene extracted the TTA—cobalt complex over a very narrow range of pH, and chloroform extracted the complex incompletely. Methyl ethyl ketone and n-butanol extracted the TTA-cobalt complex well over quite a wide pH range (5–8·5).

As is well known, the acetylacetonates of bivalent cobalt and nickel are not extracted by chloroform or even by acetylacetone;[2,7,8] methods of separating iron and other elements from cobalt and nickel are based on this. Experiments were made on the extraction of cobalt ($6{\cdot}8 \times 10^{-6}M$) with $0{\cdot}1M$ solutions of acetylacetone in benzene, n-butanol, methyl ethyl ketone, cyclohexanone, and pure acetylacetone. It was found that about 50% of the cobalt was removed in one extraction with n-butanol (pH 8–9). The cobalt was not appreciably extracted by benzene.

The influence of the nature of the diluent on the extraction of the 1-nitroso-2-naphthol-cobalt complex was studied. This chelate compound is extracted to the same extent by both active oxygen-containing solvents and non-oxygen-containing solvents such as, for example, benzene.

Chelate compounds of neptunium^{V} and uranium^{VI}

The influence of the nature of the solvent on the extraction of the thenoyltrifluoroacetonate of quinquevalent neptunium[9] was studied in detail. The neptunium was used in indicator amounts (^{239}Np), and the concentration of the TTA in the organic solvents was 0·01*M*. The results are given in Fig. 2. The best solvents for the thenoyltrifluoroacetonate were alcohols—isobutyl, n-butyl, isoamyl, and hexyl. Cyclohexa-

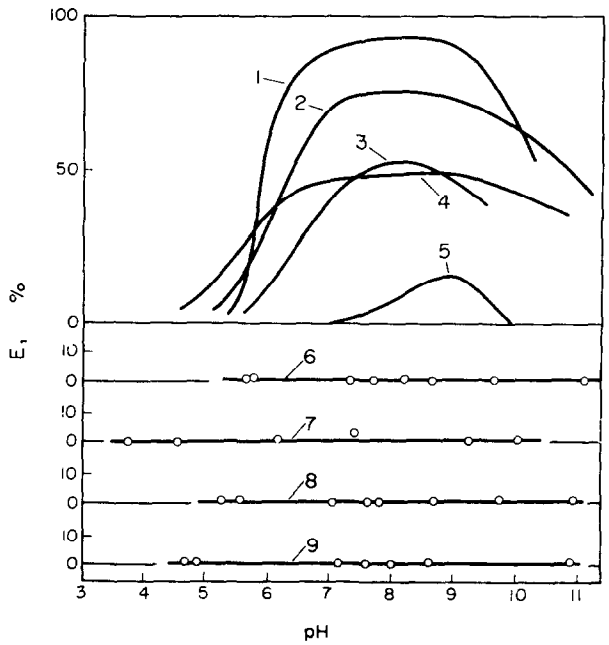


FIG. 2. Extraction of neptunium^{V} thenoyltrifluoroacetonate:
1—isobutanol; 2—cyclohexanone; 3—ethyl acetate; 4—methyl ethyl ketone; 5—amyl acetate; 6—benzene; 7—chloroform; 8—carbon tetrachloride; 9—diethyl ether.

none and methyl ethyl ketone also extracted neptunium, but not as completely as the alcohols. Neptunium was extracted by esters—ethyl acetate and amyl acetate—approximately as well as by the ketones, or slightly less well. Ethers (di-isopropyl ether), halogen-substituted hydrocarbons (dichloroethane, chloroform, carbon tetrachloride) and hydrocarbons (benzene, heptane), did not extract neptumiun.

Roughly the same dependence of the extraction of the nature of the solvent was observed in the case of the hydroxyquinolinate and the acetylacetonate of quinquevalent neptunium.

The influence of the nature of the solvent on the extraction of the 1-nitroso-2-naphthol complexes of uranium^{VI} and neptunium^{V} was also studied. It was shown that these complexes are best extracted by alcohols and ketones, and considerably less well by ethers or by hydrocarbons and their halogen-substituted derivatives.

*Hydroxyquinolates of thallium^{I} and thallium^{III}**

The hydroxyquinolinate of thallium^{I} is extracted well by isobutanol, but is not appreciably extracted by diethyl ether or carbon tetrachloride (initial concentration of

* In association with V. V. Bagreyev.

thallium in the aqueous phase $3{\cdot}9 \times 10^{-5}M$, concentration of hydroxyquinoline in the solvent $0{\cdot}05M$). See Fig. 3.

The hydroxyquinolinate of thallium^{III}, however, is extracted equally well by alcohols or ketones on the one hand, or by carbon tetrachloride on the other hand.

Chelate compounds of the rare-earth elements and iron

The thenoyltrifluoroacetonate of tervalent cerium (^{144}Ce with carrier) is extracted almost equally completely by isobutyl alcohol, cyclohexanone, and benzene; the

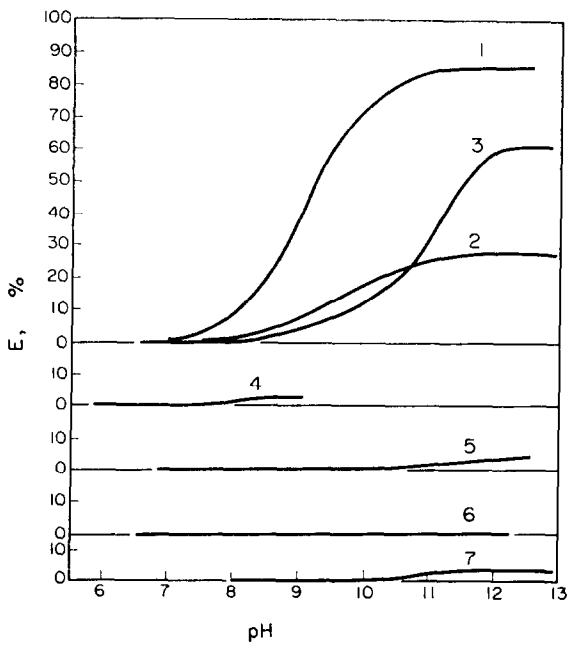


FIG. 3. Extraction of thallium^{I} hydroxyquinolinate:
1—isobutanol; 2—methyl ethyl ketone; 3—chloroform; 4—ethyl acetate; 5—carbon tetrachloride; 6—heptane; 7—diethyl ether.

extraction of the complexes of the lanthanons and TTA, using a benzene solution of the reagent, has been reported in the literature earlier.[10,11] The acetylacetonate of cerium^{III} is extracted by isobutanol, benzene, and methyl ethyl ketone. The hydroxyquinolinate of lanthanum is extracted to about the same extent by n-butanol and benzene (Fig. 4; it can also be seen that, on the other hand, barium is extracted to a somewhat greater extent by n-butanol).

The acetylacetonate of tervalent iron is extracted to a similar extent by alcohols and by benzene.

Tungsten hydroxyquinolinate

It has been noted earlier that tungsten hydroxyquinolinate is difficult to extract.[5,27,28] The present work has shown, however, that it is only macro amounts of tungsten which are poorly extracted; for example, at a concentration of $(NH_4)_2WO_4$ of approximately $10^{-3}M$, the extraction of the tungsten by benzene or n-butanol at the optimum pH of 5–7 is approximately 30–40%. On the other hand, indicator amounts

of tungsten (less than $10^{-7}M$) are extracted well. Several solvents—chloroform, benzene, amyl acetate, methyl propyl ketone, and n-butanol—were investigated. Fig. 5 gives the results for three solvents; the extraction curves for the other solvents

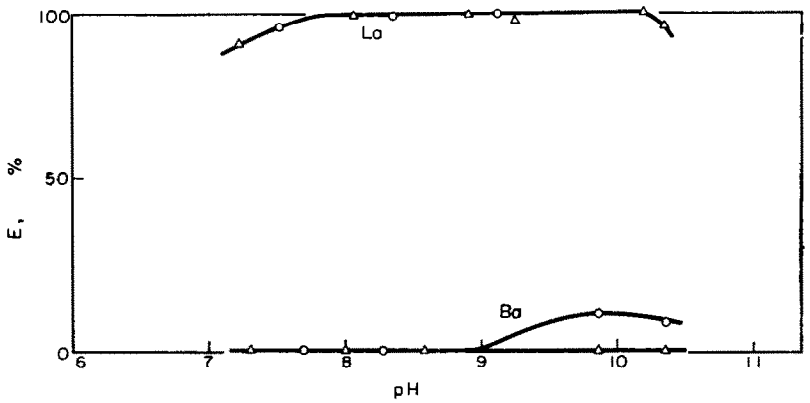


FIG. 4. Extraction of lanthanum and barium hydroxyquinolinates:
○—butanol; △—benzene.

are similar. The nature of the solvent, as can be seen from the figure, has practically no influence on the extraction. Minima similar to those which we have described elsewhere[12] can be seen on the extraction curves.

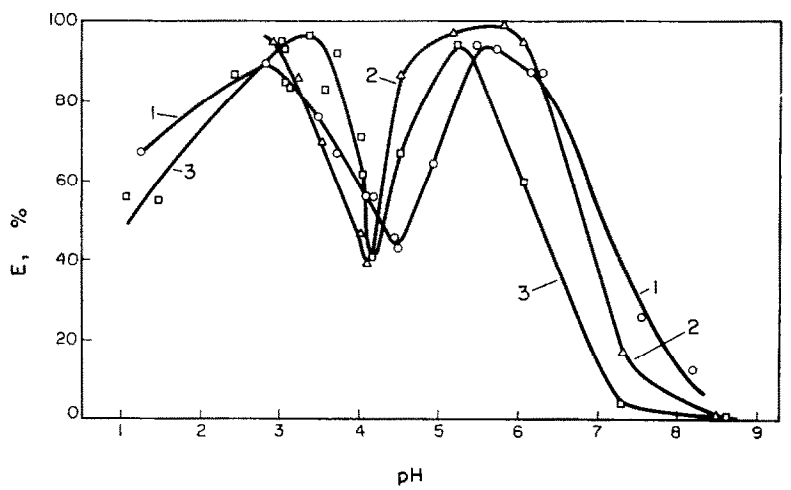


FIG. 5. Extraction of tungsten^{VI} hydroxyquinolinate:
1—n-butanol; 2—chloroform; 3—benzene.

DISCUSSION OF THE RESULTS

The results obtained show that in respect of the influence of the nature of the solvent on their extraction, chelates fall into two groups. The extraction of the chelates of the first group (the chelates of Np^{V}, Co^{II}, Tl^{I}, U^{VI}, Ba) depends quite strongly on the nature of the solvent; these chelates, as a rule, are extracted better by

polar oxygen-containing solvents, particularly alcohols, and considerably less well by non-oxygen-containing solvents of low polarity, for example, hydrocarbons and their halogen-substituted derivatives. The dependence of the extraction on the nature of the solvent proves to be very considerable in a number of cases—some chelates are extracted completely by certain solvents and are not extracted at all by others. The chelate compounds of the second group (chelates of Ce^{III}, La, Fe^{III}, Tl^{III}, W^{VI}, Co^{III}) are extracted by solvents of different types—both active oxygen-containing solvents and non-oxygen-containing solvents of low polarity.

The theoretical conclusions reached earlier,[9,13] on the dependence of the extraction of chelates on the co-ordination number of the central atom, are capable of explaining the results obtained.

On the basis of the ratio of the valency and the co-ordination number of the central atom, chelate compounds with bidentate reagents can be divided into "co-ordination-saturated" and "co-ordination-unsaturated" compounds. If the co-ordination number of the central atom does not exceed twice its charge, the chelate compound generally has no free co-ordination positions, and the central atom is completely screened by the ligands ("co-ordination-saturated" chelates); if the co-ordination number of the central atom is more than twice its charge, then the chelate *may* retain free co-ordination positions, which, in the general case, are occupied by molecules of water ("co-ordination-unsaturated" chelates).

The hydrated "co-ordination-unsaturated" chelates are normally extracted poorly. In order to make the extraction effective, it is necessary to displace the water (or "block" it by means of hydrogen bonds) using for this purpose the molecules of some organic substance. Such molecules, in the particular case, may be the molecules of an organic solvent; "active" solvents capable of co-ordination (mainly oxygen-containing solvents) readily displace the water, and they extract "co-ordination-unsaturated" chelate compounds better than "poorly-active" non-oxygen-containing solvents. "Co-ordination-saturated" chelates are capable of being extracted by solvents of extremely diverse types, including "non-active" solvents—*e.g.*, hydrocarbons or their halogen-substituted derivatives.

It can readily be seen that among the chelates which we have studied, those which are characterised by a marked influence of the nature of the solvent on the extraction can be classed as "co-ordination-unsaturated". In aqueous solutions, Np^{V} forms the cation NpO_2^+, which, it is assumed,[14] has a co-ordination number of six. A co-ordination number of 6 may also be accepted[15] for UO_2^{2+}; a co-ordination number of 6 is also found, in a number of cases, for Co^{II}; Tl^{I} is capable of exhibiting a co-ordination number of more than two.

On the other hand, the tervalent lanthanons with a co-ordination number of 6 evidently form "co-ordination-saturated" chelates; the "co-ordination-saturated" chelates also include, obviously, Fe^{III} acetylacetonate and the hydroxyquinolinates of W^{VI} and Tl^{III}. The behaviour of Co 1-nitroso-2-naphtholate as a "co-ordination-saturated" compound is a consequence of the fact that, as is well known, in this compound the cobalt is present in the tervalent state (co-ordination number equal to twice the charge). These chelates are extracted by solvents of various types, including benzene. It is obvious that the widespread point of view that the nature of the solvent does not play an essential role in the extraction of chelate compounds is correct only with respect to this particular group of chelates.

In order to ensure the extraction of "co-ordination-unsaturated" chelates, it is desirable to use a pure active solvent which is capable of co-ordination, or which binds water. This solvent can be used as an additive to an inert solvent, for example benzene, and solvents will be suitable for this which cannot be used for extraction in the pure form—*e.g.*, ethyl alcohol, dioxan, acetone, and some amines.[3,4]

In a number of cases, when an excess of the reagent is present, the "co-ordination-unsaturation" of the central atom can be satisfied by the addition of supplementary molecules of the reagent (the formation, for example, of MeR_3^-). When polydentate reagents are used, the free co-ordination positions of the central atom are occupied by the donor atoms present in the molecule of the reagent. In these cases, the chelates may be extracted with inactive non-oxygen-containing solvents—*e.g.*, carbon tetrachloride, *etc.* A tridentate derivative of 8-hydroxyquinoline has been reported which enables calcium to be extracted with chloroform without the addition of primary amines, which favour the extraction of the simple hydroxyquinolinate.[16]

There are a number of cases in the literature which, like the results of these experiments, also confirm these conclusions.

The uranyl ion is predominantly extracted by solvents with a hydrophilic group; this relates, for example, to the complex with TTA.[1] The uranyl salicylate complex is extracted by methyl isobutyl ketone under definite conditions, but is not extracted by chloroform.[17] Besides solvation by the methyl isobutyl ketone, the partial addition of a supplementary molecule of acid also takes place in this case. On extracting the complex of uranium^{VI} with β-isopropyltropolone (HT), in $CHCl_3$ the complex UO_2T_2 (HT) predominates in the organic phase; however, in oxygen-containing solvents, such as methyl isobutyl ketone, the extracted complex does not apparently contain a molecule of HT in excess.[18] The hydroxyquinolinates of the alkaline-earth metals (co-ordination number 6 or 8) are extracted poorly by chloroform, since they contain two molecules of water. These hydroxyquinolinates, however, may be extracted into the organic phase if an excess of the reagent is employed and a solvent capable of co-ordination is used. Dyrssen[21] succeeded in extracting strontium hydroxyquinolinate containing four molecules of oxine per atom of strontium in the presence of a considerable excess of the reagent (about 1*M*). Mg^{22} and Ca^{23} have been extracted when a high concentration of hydroxyquinoline (3%) was used and a co-ordinating solvent—Butyl Cellosolve—was added to the chloroform layer; if the usual conditions for the extraction of hydroxyquinolinates are employed—a 1% solution of the reagent and chloroform as the extractant—Mg, Ca, and Sr are not extracted. Be hydroxyquinolinate is extracted considerably less well by methyl isobutyl ketone than by chloroform.[29] The hydroxyquinolinates of bivalent metals are extracted well in the presence of primary amines (see, *e.g.*, refs. 3, 4, 24). The complex of Sr with perfluorooctanoic acid is not extracted by carbon tetrachloride but is extracted by methyl isobutyl ketone or isopropyl alcohol.[18]

On the other hand, Al hydroxyquinolinate ("co-ordination-saturated" chelate compound) is extracted by benzene, chloroform, carbon tetrachloride, petroleum ether, isoamyl alcohol, and butyl acetate, although best, apparently, by carbon tetrachloride.[25] Sudo[26] obtained similar results. The acetylacetonates of Ni^{II} and Co^{II} are not extracted even by acetylacetone itself, as has already been mentioned;[2] on the other hand, the acetylacetonate of cobalt which has been oxidised to Co^{III} (co-ordination number 6) is extracted well by an excess of the reagent. It is known

that many internal complex compounds of quadrivalent elements are extracted by carbon tetrachloride, benzene or chloroform.

Attention may be drawn to the possibility of separating "co-ordination-saturated" chelate compounds from "co-ordination-unsaturated" compounds. The process of separating a pair of cations, one of which yields a "co-ordination-saturated" and the other a "co-ordination-unsaturated" chelate compound with a given reagent, consists in extracting the "co-ordination-saturated" chelate with a solution of the reagent in an inactive solvent—*e.g.*, benzene—at an appropriate pH. Under these conditions, the "co-ordination-unsaturated" chelate compound may, in some cases, remain completely unextracted. Then, sometimes at the same pH, the "co-ordination-unsaturated" chelate is extracted with an active solvent—*e.g.*, butanol—if this is necessary.

We have studied the possibility of separating quinquevalent neptunium and the lanthanons by extracting the thenoyltrifluoroacetonates. Since the pH ranges for the extraction of Np^{V} and, for example, $cerium^{III}$ are similar, it is impossible to separate them by changing the pH. Both thenoyltrifluoroacetonates are readily extracted by isobutanol, but benzene only extracts the Ce.

Acknowledgements—The authors express their thanks to V. V. Bagreyev and G. A. Vorob'eva for their assistance in carrying out the experiments.

Zusammenfassung—Der Einfluss des organischen Lösungsmittels in der Extraktion der Thenoyltrifluoroacetonate von Np^{V}, Co^{II} und Ce^{III}, der Hydroxyquinolate von Np^{V} und Fe^{III}, des 1-Nitrose-2-naphtholates von Co^{II}, und von einigen anderen Chelaten, wurde untersucht. In der Regel werden "koordinationsungesättigte" Chelate (d.h. solche mit Koordinationszahl des Zentralatoms grösser als zweimal dessen Ladung) besser durch Ketone, Ester, und besonders Alkohole, und schlechter durch Äther, Kohlenwasserstoffe und halogenierte Kohlenwasserstoffe extrahiert. In einigen Fällen wird die Extraktion dieser Chelate durch einen Uberschuss des Koordinationsmittels begünstigt. "Koordinationsgesättigte" Chelate (d.h. solche mit Koordinationszahl des Zentralatoms kleiner als zweimal dessen Ladung) werden dagegen durch Lösungsmittel mancher Art, z.B. sauerstofffreie, schwach polare Lösungsmittel, extrahiert. Es wird auf die Möglichkeit hingewiesen, "koordinationsgesättigte" Chelate von den Koordinationsungesättigten" zu trennen.

Résumé—Les auteurs étudient l'influence de la nature du solvant organique sur l'extraction des thénoyltrifluoroacétonates de Np(V), Co(II) et Ce(III), des oxinates de Np(V) et W(VI), des acétylacétonates de Co(II) et Fe(III), du 1-nitroso-2-naphtolate de Co et de quelques autres complexes. Il est montré qu'en regle générale les complexes à coordinance insaturée (indice de coordinence de l'atome central supérieur au double de sa charge) sont extraits préférentiellement par les cétones, les esters et, tout particulierement, par les alcools, tandis qu'ils le sont moins bien par les éthers, les hydrocarbures et leurs dérivés hologénés. L'extraction de ces complexes peut, dans certains cas, être améliorée par l'utilisation d'un exces de réactif. Les complexes à coordinence saturée (indice de coordinence de l'atome central inférieur ou égal au double de sa charge) peuvent être extraits par des solvants de nature très diverse, entre autre par des solvants non oxygénés de polarité relativement faible. Il en résulte des possibilités de séparation des complexes à coordinence saturée et à coordinence insaturée.

REFERENCES

[1] D. Dyrssen, *Svensk. Kem. Tidskr.*, 1956, **68**, 212.

[2] G. H. Morrison and H. Freiser, *Solvent Extraction in Analytical Chemistry*. New York, John Wiley and Sons, 1957.
[3] F. Umland and W. Hoffmann, *Angew. Chem.*, 1956, **68**, 704.
[4] F. Umland and K. -U. Meckenstock, *Z. analyt. Chem.*, 1959, **165**, 161.
[5] V. Dziomko, *Sbornik statei Vsesoyuznogo zaochnogo politekhnicheskogo instituta* [*Collection of Papers of the All-Union Correspondence Polytechnical Institute*]. No. 4, 1953, p. 44.
[6] S. K. Majumdar and A. K. De, *Z. analyt. Chem.*, 1960, **177**, 97.
[7] M. Tabushi, *Bull. Inst. Chem. Res. Kyoto Univ.*, 1959, **37**, 232, 252.
[8] W. B. Brown and J. F. Steinbach, *Analyt. Chem.*, 1959, **31**, 1805.
[9] Yu. A. Zolotov and I. P. Alimarin, *Radiokhimiya*, 1962, **4**, 272.
[10] T. K. Keenan and J. F. Suttle, *J. Amer. Chem. Soc.*, 1954, **73**, 2184.
[11] E. Hyde, *Proc. Intern. Conf. Peaceful Uses of Atomic Energy*, Geneva, 1955, Vol. 7.
[12] I. P. Alimarin, O. M. Petrukhim and Yu. A. Zolotov, *Zhur. analit. khim.*, 1962, **17**, 544.
[13] Yu. A. Zolotov and I. P. Alimarin, *Dokl. Akad. Nauk SSSR*, 1961, **136**, 603.
[14] K. A. Kraus, F. Nelson and G. L. Johnson, *J. Amer. Chem. Soc.*, 1949, **71**, 2510.
[15] I. I. Lipilina, *Uranyl i ego soyedineniya* [*Uranyl and its Compounds*]. *Izd. Akad. Nauk SSSR*, Moscow, 1959.
[16] F. Umland and K. -U. Meckenstock, *Angew. Chem.*, 1959, **71**, 373.
[17] B. Hök-Bernström, *Svensk Kem. Tidskr.*, 1956, **68**, 34.
[18] D. Dyrssen, *J. Inorg. Nucl. Chem.*, 1958, **8**, 291.
[19] W. S. Horton, *J. Amer. Chem. Soc.*, 1956, **78**, 897.
[20] W. E. Clifford, E. P. Bullwinkel, L. A. McClaine and P. Joble, *ibid.*, 1958, **80**, 2959.
[21] D. Dyrssen, *Svensk Kem. Tidskr.*, 1955, **65**, 43.
[22] C. L. Luke, *Analyt. Chem.*, 1956, **28**, 1443.
[23] C. L. Luke and M. E. Campbell, *ibid.*, 1954, **26**, 1778.
[24] F. Umland, W. Hoffmann and K. -U. Meckenstock, *Z. analyt. Chem.*, 1960, **173**, 211.
[25] M. M. Raines and Yu. A. Larionov, *Zavodskaya Lab.*, 1948, **14**, 1000.
[26] E. Sudo, *Z. analyt. Chem.*, 1953, **138**, 275.
[27] F. G. Zharovskii, *Ukrainskii khim. Zhur.*, 1951, **17**, 64.
[28] J. P. Riley, *Analyt. Chim. Acta*, 1959, **21**, 317.
[29] H. Gotô and Y. Kakita, *J. Chem. Soc. Japan, Pure Chem. Sec.*, 1959, **80**, 1448.

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AN I-Q RECORDER AND ITS APPLICATION TO RAPID COULOMETRIC ANALYSIS AND MICRO-COULOMETRY

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Summary—The author recently described a direct-reading current integrator and subsequently improved it into a recording instrument, the I–Q recorder. It can be used not only for coulometric analysis but also for other purposes. The highest sensitivity range is 10 μA; the reproducibility can be assumed to be 0·1%. Integration is possible from input zero to rated value. Rapid determination of micro amounts of copper and lead, 1–10 μg and 4–10 μg respectively, has been carried out. Rapid determination of 0·9 mg of lead and 0·8 mg of cadmium from their mixtures is discussed.

INTRODUCTION

CONTROLLED potential coulometric analysis has been studied by several groups of workers in recent years. Of these studies, a great many are concerned with instrumentation. A possible explanation for this fact is that first, no suitable instrument has been produced; secondly, instrumentation in this field is difficult. Current integration, however, is one of the very important techniques in routine chemical analyses. Besides its application to coulometric analysis, it can be applied to other routine instrumental analyses, such as integration in gas chromatography and intensity integration in spectrophotometry. It can also be applied to research technique in physical chemistry.

In controlled potential coulometric analysis, according to Lingane,[1] the electrolysis current which is integrated decreases exponentially. For the integration of such a current which varies, a suitable integrator is required. Such an integrator can also be used for constant current coulometric titration. However, the current-time technique of constant current coulometric titration cannot be used for controlled potential technique. Thus an integrator for controlled potential coulometric analysis has wide use. Devices which can also be used for both techniques are chemical coulometers,[2] electromechanical integrators[3,4,5] and the method of calculating from the current-time curve.

The author has previously described a direct-reading current integrator[6] which employs a bevel gear differential and a tachogenerator for standardisation. The advantage of this integrator is that it has several good characteristics of which high output power and high sensitivity are the most important. These advantages made possible the development of the I-Q recorder. As previously described in a preliminary report,[7] rapid coulometric analysis can be achieved by using this type of recorder. Because of its high sensitivity, micro-coulometric analysis of samples in concentrations of 10^{-6}–$10^{-7}M$ can be carried out using the same technique as that used for macro-coulometric analysis.

EXPERIMENTAL

Apparatus

The I–Q recorder is basically the same as the integrator used in previous reports.[7] In the direct-reading current integrator, the measured integration of current was recorded digitally. The major difference in this I–Q recorder, however, is that the chart is driven by the measured number of coulombs and the number of coulombs corresponds to the recorded chart length. On this I–Q recorder chart, the horizontal axis (normally the time axis) indicates the amount of electricity, Q. The vertical axis can indicate any type of signal, *e.g.*, pH, potential, current. In the present case, the electrolysis current, i, is indicated on the vertical axis. Therefore, this I–Q recorder chart indicates electrolysis current, i, against amount of electricity, Q. High sensitivity and rather large driving power are requisites for this recorder. To obtain these requisites, an a.c. amplifier is employed. A standard frequency source using a crystal oscillator drives the synchronous motor which supplies one input to the bevel gear differential causing it to rotate at constant speed.

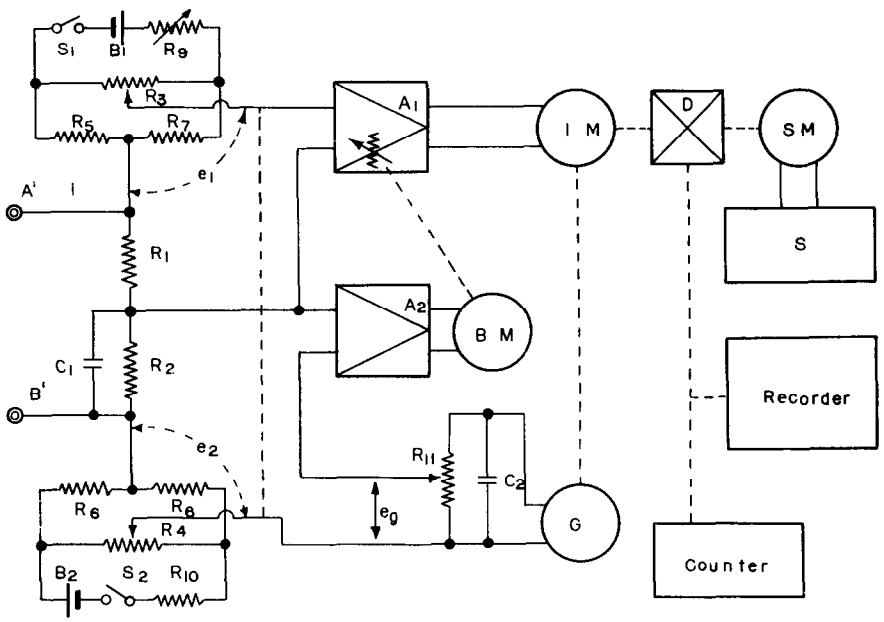


FIG. 1.—Block diagram of coulometer.

A_1:	input amplifier	$R_{1,2}$:	5-kΩ (manganin wire winding)
A_2:	deviation amplifier	$R_{3,4}$:	1-kΩ gang variable resistor
IM:	integrating motor	$R_{5,6,7,8}$:	250-Ω
BM:	servomotor	R_9:	10-kΩ variable resistor
SM:	synchronous motor	R_{10}:	5-kΩ
G:	tachogenerator	R_{11}:	1-kΩ
D:	differential gear	C_1:	10 μF
S:	constant frequency source	C_2:	0·01 μF

Fig. 1 shows a block diagram of the present I–Q recorder. The characteristic curve of the input voltage of IM versus rotating speed is indicated in Fig. 2. Only the linear portion of this curve is utilised by IM. The output axis of the differential gear is mechanically connected to the counter and also to the driving device of the recorder chart. This current integrator circuit can be used to drive many mechanisms requiring rather large driving power. The I–Q recorder was made possible because of this characteristic.

The synchronous motor SM supplies 10 rpm to the differential gear mechanism. When the measured current is zero, the integration motor IM must rotate at 10 rpm. For this purpose, a suitable voltage, e_1, produced by a mercury cell and variable resistor, is always supplied to the input of amplifier A_1 regardless of the measured current. Tachogenerator G, connected to IM by gears, possesses e.m.f. even when the measured current is zero; this tachogenerator voltage is applied to

amplifier A_2. Another mercury cell and variable resistor produce a voltage, e_2, which is applied to amplifier A_2 in a similar manner to that in the case of A_1. Here, applied voltage e_2 equals the generated voltage from the tachogenerator when the measured current is zero. For zero adjusting, the voltage of e_1 is changed; similarly, voltage e_2 must be altered accordingly. Under suitable conditions e_1 can be made to equal e_2 by which handling becomes easy. Thus a gang variable resistor is used to keep e_1 equal to e_2 at all times.

To explain further:

$$e_g = KA'(iR_1 + e) \tag{1}$$

where e_g is the e.m.f. of the tachogenerator, A′ is the amplification factor, i is the electrolysis current, and K is a constant. The voltage of the detective circuit shows

$$iR_2 + e_2 \tag{2}$$

This device has an automatic control circuit which operates to make equation (1) equal equation (2). From this condition:

$$KA' = \frac{iR_2 + e_2}{iR_1 + e_1} \tag{3}$$

When i is zero:

$$KA' = \frac{e_2}{e_1} \tag{4}$$

From equations (3) and (4):

$$\frac{e_2}{e_1} = \frac{R_2}{R_1} \tag{5}$$

R_1 and R_2 are input resistors and e_1 and e_2 are variable voltages. A gang variable resistor and cells are used to keep ratio R_1/R_2 equal. When K, a ratio of input voltage of the integrating motor and

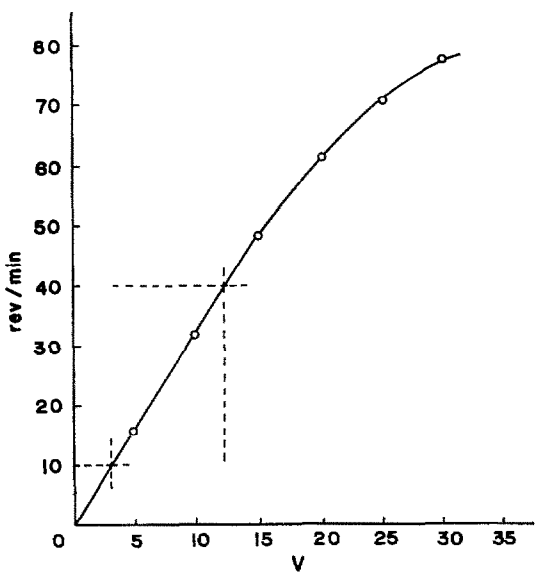


FIG. 2.—Characteristic curve of integration motor.

e.m.f. of the tachogenerator, becomes constant, the automatic control circuit does not operate. In the linear condition of the integrating motor, K is constant; however, when the rotation speed of the motor is decreased although the input speed remains unchanged, K becomes smaller and amplification factor A′ of amplifier A_1 must be made larger. Only in this case the automatic control circuit changes amplification factor A′. During good conditions the automatic control circuit need not operate. Consequently the response of this coulometer is good.

Tachogenerator

The present apparatus employs a d.c. tachogenerator because the measured current is d.c. and is compared with the e.m.f. of the tachogenerator. A d.c. motor, a battery-clock motor, was used for the

tachogenerator.* The internal resistance of this motor was 1 kΩ, and the e.m.f. was 4 mV/1 rpm. The linearity was 0·1 % in the range of 30–120 rpm. The filter circuit was a 0·01-μF condenser which supressed the high frequency noise voltage.

Characteristic of e.m.f. versus revolution of tachogenerator

To measure this characteristic curve accurately, a constant speed motor and gears were used. A synchronous motor was used for the constant speed motor and was supplied by a crystal constant frequency source. Thus the deviation of revolution was within 10^{-3}–10^{-4} %. The gear ratios were changed and the following speeds, 9·885, 19·779, 30·000, 45·498, 60·000, 90·999, 120·000, 181·998 rpm, were used for driving the generator.

Table 1 shows the character of the tachogenerator in the range for actual use and shows e.m.f./1 rpm. To check long-range stability, the measurements were taken on different days, as represented by the numbers in the first column. The standard deviation was under 0·1 %. With regular d.c.

TABLE I.—LINEARITY OF TACHOGENERATOR

No. \ rpm	120·000	90·999	60·000	45·498	30·000	mean
1	3·809	3·809	3·813	3·803	3·803	3·807
2	3·808	3·810	3·808	3·803	3·803	3·806
3	3·811	3·811	3·809	3·802	3·802	3·807
4		3·811	3·808	3·807	3·807	3·808
5		3·809	3·813	3·805	3·803	3·808
mean	3·809	3·810	3·810	3·804	3·804	3·807

Numbers in table show mV/rpm.

tachogenerators, the linearity was 0·25 %; but this tachogenerator has a linearity of 0·1 %, because the revolution range used is narrow. One advantage of this coulometer is that only the range with the best linearity can be used.

Integration motor and amplifier

The integration motor requires the following characteristics: (1) Characteristic curve of input voltage *vs.* revolution speed must be linear and long. (2) Inertia of rotor must be small, which contributes to better response. (3) During use, change in motor character must be small. The author used a 2-phase a.c. motor.† Fig. 2 shows the characteristic curve of this motor: input voltage *vs.* revolution speed. The integrating motor of this coulometer has an input voltage in the range of 3·5–12 V. This range is almost linear.

Revolution and its control are performed by the amplifier in Fig. 3. This amplifier requires linearity of input and output voltages. In this condition, integration motor speed is in direct proportion to input voltage. If the character of the amplifier is not linear, the response of the integration motor becomes bad, because motor speed and input voltage are not proportional and time is required to change the amplifier gain. This amplifier has a rated input voltage of 50 mV and uses an output transformer with a primary coil impedance of 5 kΩ and a secondary coil impedance of 500 Ω. The transformer is designed so that the secondary coil impedance is smaller than the control coil impedance of the motor; this improves the motor response.

Constant frequency source

Synchronous motor speed N_s is in direct proportion to frequency f of driving source:

$$N_s = \frac{120}{p} f \quad \text{(rpm)}$$

where p is the number of poles of the motor. A crystal oscillator‡ supplies the standard frequency of this source which has a character of 60 c/sec, 100 V, precision 10^{-5} %.

* Nippon Denki Tokei Co., Japan.

† Tamagawa Seiki Co., Japan, Type TS 93: output power 3·5 W; 2,700 rpm—no load; exciting current 0·17 A; control current 0·22 A; exciting coil impedance 860 Ω; control coil impedance 680 Ω; gear ratio 1/30.

‡ Toyo Tsushinki Co., Japan, Type TCO–1, natural frequency 12 kc/sec, output frequency 60c/sec by transistor frequency divider.

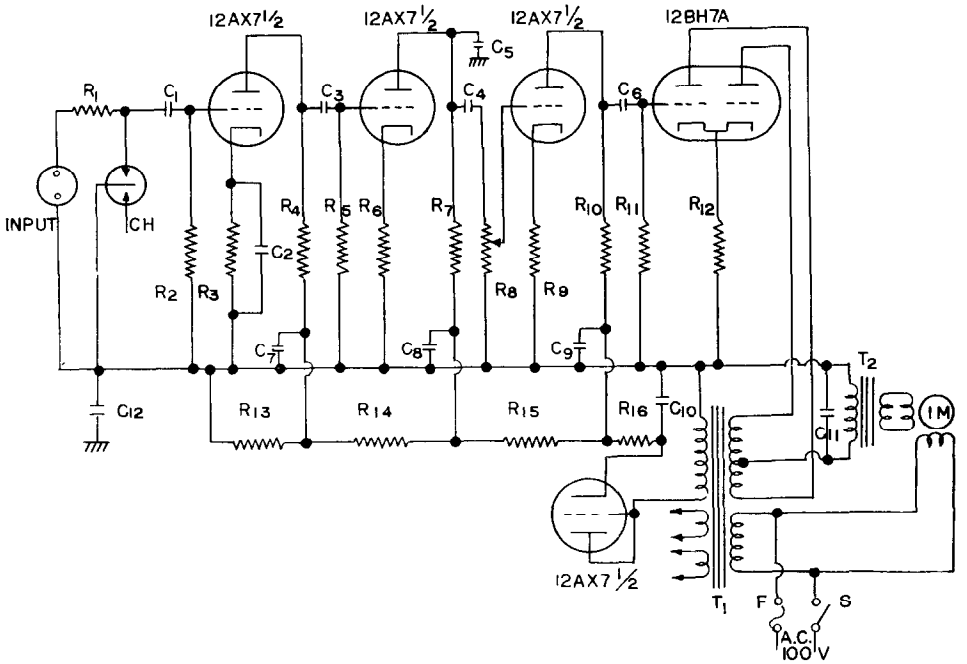


FIG. 3.—Amplifier for integrating motor.

R_1:	1 mΩ	R_9:	20 kΩ	C_1:	0·01 μF	C_9:	20 μF
R_2:	500 kΩ	R_{10}:	500 kΩ	C_2:	10 μF	C_{10}:	20 μF
R_3:	3 kΩ	R_{11}:	500 kΩ	C_3:	0·05 μF	C_{11}:	2 μF
R_4:	500 kΩ	R_{12}:	500 Ω	C_4:	0·05 μF	C_{12}:	200 μF
R_5:	1 mΩ	R_{13}:	200 kΩ	C_5:	0·01 μF		
R_6:	20 kΩ	R_{14}:	100 kΩ	C_6:	0·1 μF		
R_7:	500 kΩ	R_{15}:	50 kΩ	C_7:	20 μF		
R_8:	500 kΩ	R_{16}:	10 kΩ	C_8:	20 μF		

T_1: Transformer

T_2: Output transformer, P. 5 KΩ, S. 500 Ω IM: Integrating motor (2 phase, 2 pole)

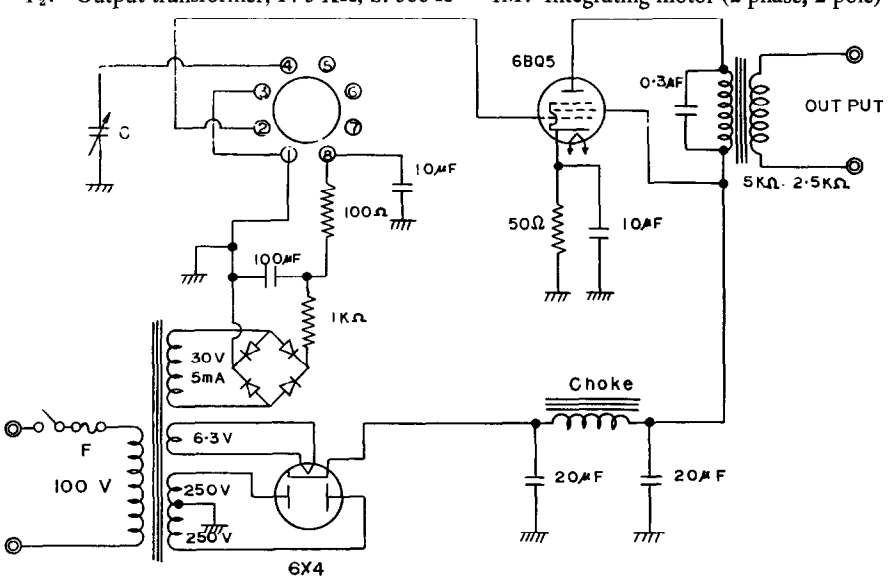


FIG. 4.—Constant frequency source.

Input supplement circuit

The conditions designated in equation (5) must be attained to have this device operate perfectly. Voltage drop iR_1 is supplied to the amplifier and iR_2 is the reference voltage for error detection; R_1 and R_2 do not require absolute values, but these values must be constant. For this purpose, material with low temperature coefficient, manganin wire, is used for the resistors. This coulometer is designed so that the maximum sensitivity of rated current is 10 μA and the maximum input of the amplifier requires about 50 mV; therefore R_1 must be 5 kΩ. R_2 is independent of R_1; but since iR_2 is compared with the e.m.f. of the tachogenerator, the value of R_2 is dependent upon the e.m.f. of the tachogenerator. The ratio of R_1 and R_2 in equation (5) is given an arbitrary value.

To facilitate the making and adjusting of this coulometer, R_1 was made equal to R_2 equal to 5 kΩ. Thus e_1 equals e_2; these voltages must be constant at all times at the set voltage. For this purpose a mercury cell is employed. To drive the integrating motor at 10 rpm, a 20-mV input voltage is necessary and integration is zero at this point. If the electrolysis current contained a background current equivalent to the rated current, e_1 requires -30 mV, *i.e.* -20 mV minus 50 mV. This coulometer is

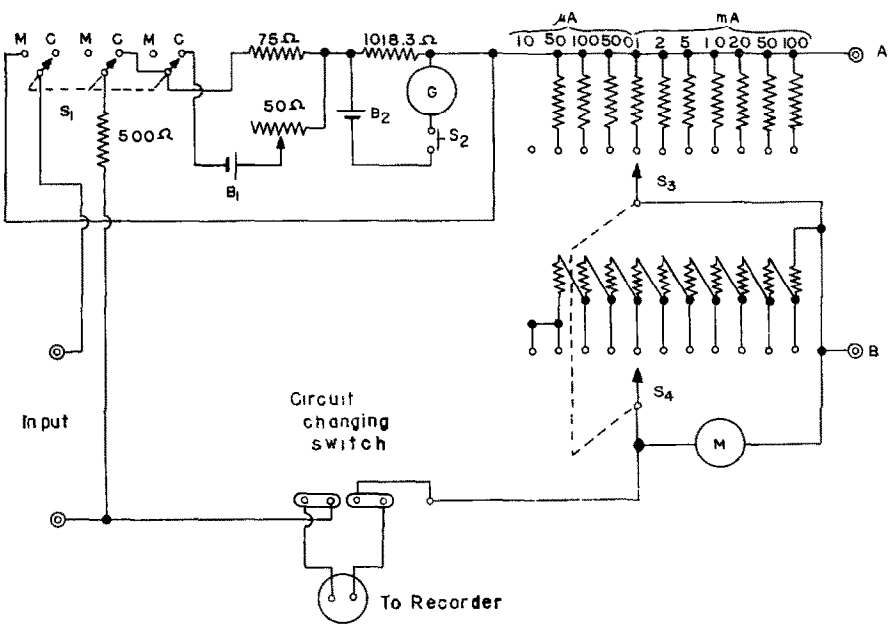


FIG. 5.—Sensitivity change and correction circuit.

adjusted to a range of ± 40 mV. In general use e_1 requires only 20 mV, but a range from $+40$ to -40 mV is used to facilitate adjusting. By this means:

$$\text{electrolysis current} \leq 2 \times \text{value of rated current}$$

provided that

$$\text{maximum integrated current} = \text{value of rated current}$$
$$\text{maximum non-integrated current} = \text{value of rated current.}$$
$$\text{(background current)}$$

To make e_1 equal to e_2, the angles of rotation of variable resistors R_3 and R_4 must be proportional to their resistances. Generally, the resistances of R_3 and R_4 are difficult to make equal; here, variable resistor R_9 is used for fine adjustment of the difference between R_3 and R_4.

Sensitivity change and correction circuit

Shunt resistors spanning over R_1 and R_2 are used for sensitivity changing. S_3 is an eleven-range switch with the following rated currents: 10 μA, 50 μA, 100 μA, 500 μA, 1 mA, 2 mA, 5 mA, 10 mA, 20 mA, 50 mA, 100 mA. No shunt is used in the 10-μA range. The accuracy of these shunts is not very good, but should be within 0·1–0·05%. Table II shows input voltages for each rated current. This

table is used for correction of the shunts. The characteristics of the tachogenerator influence the accuracy of this coulometer, but these characteristics may be changed during long use. The author built-in the null method standardisation circuit in the coulometer. This standardisation circuit consists of a standard cell B(1·0183 mV), standard resistor (1·0183 kΩ), galvanometer G, and produces a 1-mA standardised current. For correction of the coulometer, S_1 in Fig. 5 is switched to C, standardised

TABLE II.—CORRECTION OF SHUNTS

Range	Input voltage,* *mV*	Shunt,† *Ω*
10 μA	100·64	none
50 μA	99·875	2492·9
100 μA	99·263	1101·2
500 μA	100·58	205·30
1 mA	103·59	104·06
2 mA	99·883	50·189
5 mA	100·80	20·200
10 mA	99·927	10·002
20 mA	100·56	5·030
50 mA	100·47	2·009
100 mA	116·08	1·160

* The input voltage is a calculated value and corresponds to the value of rated current times input resistance with shunt.

† This value is calculated from rated current and input voltage.

1-mA current is passed to the integrating input, the reading is noted and the factor (count/coulomb) is obtained when

$$1 \text{ coulomb} = 1 \text{ mA} \times 1000 \text{ sec.}$$

S_3 and S_4 in Fig. 5 are gang switches which change the rated value of meter M simultaneously with the changes in sensitivity at every rated current range except the 10-μA range. When recording the I–Q curve with this device, the circuit changing switch is turned so that the electrolysis current flows to the recorder. To record the amount of electricity versus pH or other signal, the circuit changing switch is turned so that the electrolysis current is cut off from the recorder to which a suitable detector is connected.

Factor

The factor (count/coulomb) should be stable. Table III shows the deviation of this factor in the 1-mA range. Each measured value was taken once or twice each day over 1 month. In the other ranges, the factors are obtained by calculation from the factor of the 1-mA range, then corrected with the values in Table II.

TABLE III.—DEVIATIONS OF FACTOR IN 1-mA RANGE

No.	Factor,* *count/coulomb*
1	$24·99 \times 10^3$
2	$25·04 \times 10^3$
3	$25·09 \times 10^3$
4	$25·00 \times 10^3$
5	$24·98 \times 10^3$
6	$25·02 \times 10^3$
7	$24·97 \times 10^3$
8	$24·99 \times 10^3$
9	$25·00 \times 10^3$
10	$25·01 \times 10^3$
11	$25·02 \times 10^3$

* Mean: $25·01 \times 10^3$; standard deviation: $0·02 \times 10^3$; coefficient of variation: 0·08%.

TABLE IV.—ROUND NUMBERS OF FACTOR IN EACH RANGE

Range	Factor, *count/coulombs*
10 μA	2500×10^3
50 μA	500×10^3
100 μA	250×10^3
500 μA	50×10^3
1 mA	25×10^3
2 mA	$12{\cdot}5 \times 10^3$
5 mA	5×10^3
10 mA	2500
20 mA	1250
50 mA	500
100 mA	250

Recorder

In this device total revolutions of the output axis of the differential gear corresponds to the amount of electricity. This output power moves the counter and the chart-driving mechanism of the recorder. One rotation of output axis corresponds to 1800/17 count; by watching the counter needle, zero adjusting before measurement can be performed precisely. In the chart-driving mechanism, the output power is passed through 1:10 reduction gears in 2 stages to a speed change gear (0·125, 0·25, 0·375, 0·75, 1·5, 3), then through a 40:75 gear train to drive the chart. From these relations, one rotation of the output axis of the differential gear drives the chart for a length of

$$150 \text{ mm} \times 1/100 \times (\text{reduction ratio}) \times 40/75 \text{ (mm)}.$$

One count of the counter corresponds to the chart length of

$$70/2250 \times (\text{reduction ratio}) \text{ (mm/count)}.$$

The starting position of the recording pen can be adjusted to the rated value, *i.e.* electrolysis current minus background current (maximum is rated value) can be recorded.

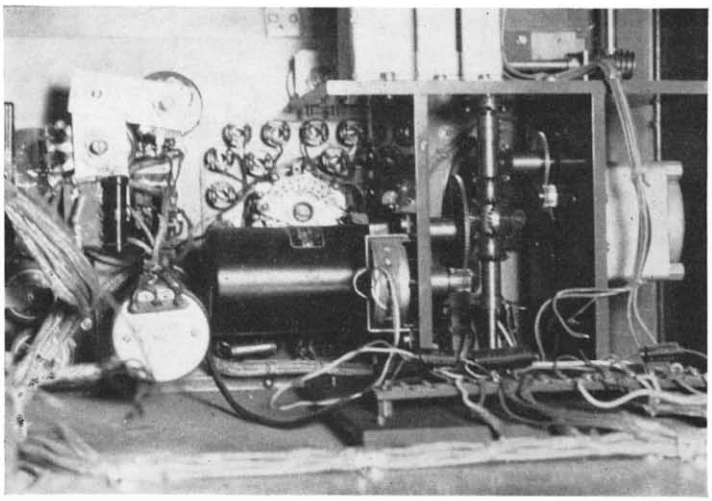
Character of coulometer

Deviation of the factor is 0·08 %(Table III). Linearity of the tachogenerator is 0·1 %. Reproducibility of this device can be assumed to be 0·1 %. When rated input is supplied to the recorder, then cut off, the counter needle moves for a distance of 2–3 counts. When rated input is supplied to the recorder for over 100 sec, the error is under 0·1 %. The counter needle remains stationary for about 20–50 min. The zero shifting (drift) has no effect on the accuracy of this coulometer.

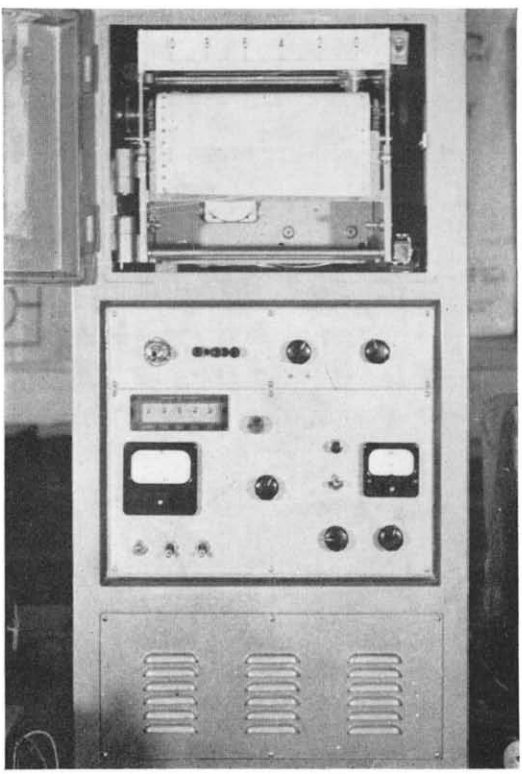
Rapid Determination of Lead and Cadmium

The first step in the experiment concerns the rapid determination of lead and cadmium from their mixtures by means of mercury cathode controlled potential coulometric analysis. Because the deposition potentials of lead and cadmium differ by 0·2 V, their separation from each other is practicable. However, successive determination of each element from one aliquot is not feasible, because the background current varies according to the function of the limited cathode potential. For instance, if after determination of lead, the cathode potential is shifted to the cadmium deposition potential, cadmium is deposited; but, because the background current cannot be measured, this is not a determination. In such a condition, successive determination of each element from one aliquot is possible only if the background current is negligibly smaller than the electrolysis current, or if a condition is found in which background current is reproducible and correction can be made. In these experiments the respective amounts of background current at each cathode potential were found before every determination by pre-electrolysis. In the actual determinations lead alone was determined first, then cadmium plus lead from another aliquot of the same sample, and hence the quantity of cadmium was calculated.

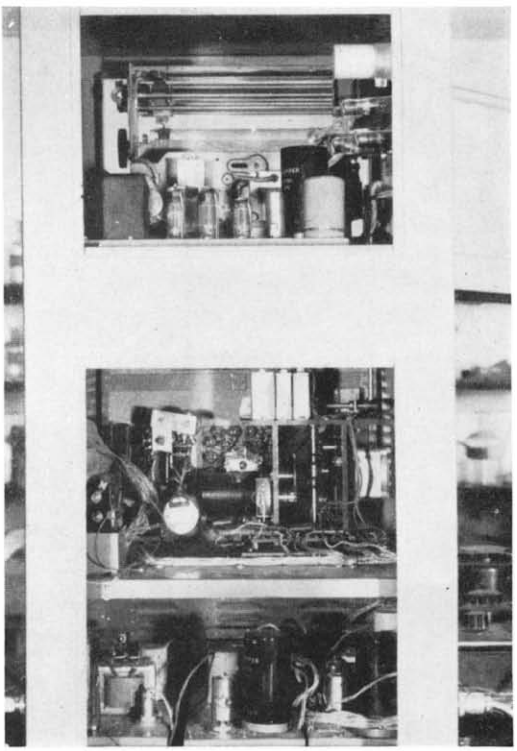
The I–Q curve is a straight line theoretically and experimentally.[7] Therefore, for determination, only the initial short length is sufficient in the recording of an I–Q curve. The inclination of the entire curve is determined by extending a line from this recorded section. By extrapolation, the estimated resultant amount of electricity Q is found at the intersection with the Q-axis.



(A)



(B)



(C)

FIG. 6.—(A) Differential gear and main mechanism.
(B) Front view of I–Q recorder.
(C) Rear view of I–Q recorder.

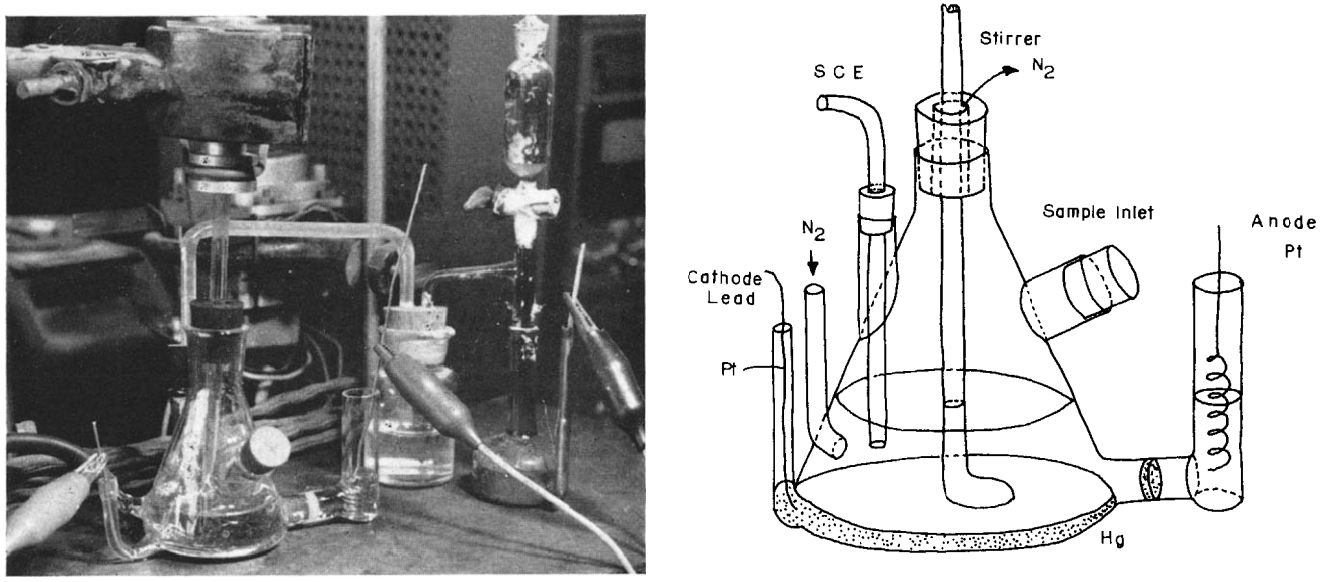


FIG. 7.—Mercury cathode electrolysis cell.

Reagents

Lead and cadmium: Standard samples were made from analytical grade lead and cadmium acetates by electrolysis.

Mercury: Distilled and used for the cathode.

Potassium chloride electrolyte: 0·5*M* potassium chloride (analytical grade) was used for the electrolyte.

Electrolysis cell

Fig. 7 shows a cell used in this experiment. The cathode chamber is made from a 50-ml Erlenmeyer flask to facilitate removal of oxygen. The volume of potassium chloride electrolyte in cathode chamber is 20 ml and in anode chamber 4 ml. The cathode mercury is 10 ml. The spiral anode is 1-mm diameter platinum wire and a sintered glass disk (10 mm diameter) is placed between the anode and cathode chambers.

Potentiostat

The Yanagimoto Seisakusho modification of the Lingane-Jones' potentiostat[10] was used.

Procedure

The cathode chamber was filled with 20 ml of 0·5*M* potassium chloride solution, and the anode chamber with 4 ml of the same solution. The mercury for the cathode, 10 ml, was added to the cathode chamber.

Nitrogen gas was bubbled through the cathode chamber for about 10–15 min before pre-electrolysing. The dissolved oxygen in the supporting electrolyte was reduced at the mercury cathode at about −0·05 V *vs.* S.C.E. Even if the oxygen removal from the supporting electrolyte is incomplete, any remaining dissolved oxygen is reduced during pre-electrolysing; this is possible because the deposition potentials of most substances are more negative than −0·05 V. Because dissolved oxygen present in the sample solution will interfere with the determination, the regular polarographic cell was employed for its removal.

The potentiostat was set at −0·55 V *vs.* S.C.E., 0·5–1 ml of "dummy" sample solution was added to the electrolysis cell, and pre-electrolysis begun and continued till the current (background current) was constant. The reason for this procedure is that the author believes that even when the background current appears constant, a certain small amount of sample remains in the electrolyte under practical conditions. At this time when the background current is constant, the unknown sample is added and the electrolysis continued till the background current again becomes constant, *i.e.* reaches the point of constance at which the unknown sample was added. In this manner the amount of unelectrolysed sample assumed to be remaining in the electrolyte after pre-electrolysing is equivalent to the small sample remaining unelectrolysed after the actual determination. As mentioned above, reproducibility of the background current becomes better, because the electrolysis conditions before and after determinations are about the same.

After this pre-electrolysis, 2 ml of sample solution were added to the cell through the sample inlet. During this addition, care must be taken to prevent the entrance of air. The I–Q curve was recorded till the inclination of the curve could be assumed. A line from the I–Q curve was extended till it crossed the straight line ab (Fig. 8). Point a is the position of the pen just before adding the sample (same position as background current). Straight line ab is parallel to the X-axis. The length of straight line ab corresponds to the amount of electricity for complete electrolysis of the lead. The same procedure was repeated with the cathode potential set at −0·75 V, and the amount of electricity was obtained. This amount of electricity corresponds to the combined amount of lead and cadmium. The amount of cadmium was then obtained by difference.

Table V shows the results of determinations of lead and cadmium.

The values shown are the means obtained from 3–5 determinations. Complete electrolysis ordinarily requires about 2 hr per sample; this rapid method requires only about 30 min per sample. Each determination had a deviation of about 0·01–0·06 mg. These rather large deviations are believed to be caused by a slight error in measurement of chart length.

Determination of Micro Amounts of Copper and Lead

Another advantage of coulometric analysis is its applicability to micro determinations, *e.g.*, the determination of 2–600 mg of copper by controlled potential coulometry using a mercury cathode with an accuracy of 0·1 %;[5] determination of $10^{-5}M$ copper using a millicoulometer;[6] determination

of $10^{-8}M$ lead using special techniques.[9] Till now the low limit for coulometric determinations has been in the range of 10^{-3}–$10^{-4}M$ (50–100 millicoulomb). The present I–Q recorder can be applied to coulometric determinations in the range of 10^{-6}–$10^{-7}M$. One point which requires careful consideration is the fact that the effect of oxygen during determinations is great. If oxygen is present in the solution in the cell, the I–Q curve shows the presence of oxygen (Fig. 9); thus, it makes possible easy detection of experimental mistakes. This is one of the advantages of the instrument. During micro determinations,

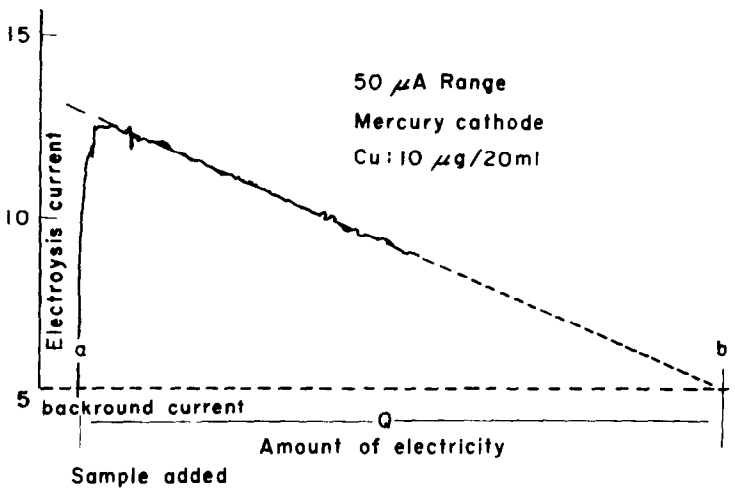


FIG. 8.—Construction of the I–Q curve.

TABLE V.—DETERMINATION OF LEAD AND CADMIUM IN MIXTURES

Sample	Present		Found (mean)		Error		
	mg	*coulombs*	*mg*	*coulombs*	*mg*	*coulombs*	%
Cd[a]	0·798	1·37	0·792	1·36	−0·006	−0·01	0·7
Pb[b]	1·785	1·66	1·815	1·69	+0·03	+0·03	1·7
Pb[c]	0·893	0·831	0·908	0·845	+0·015	+0·014	1·7
Pb + Cd[d]		2·20		2·17		−0·03	
Cd[e]	0·798	1·37	0·772	1·33	−0·023	−0·04	2·8

[a,b] Samples of cadmium and lead alone.
[c] Samples of cadmium and lead in mixtures.
[e] Calculated from (d) minus (c).

current fluctuations, which are rather large when compared with the electrolysis current, are recorded on the chart; this necessitates using a damping circuit (Fig. 10).

Removal of oxygen from sample

Oxygen dissolved in the sample was reduced at the mercury cathode at −0·05 V *vs.* S.C.E., controlled potential electrolysis; therefore, oxygen in the sample must be removed before determination. For this purpose, the author used the apparatus shown in Fig. 11. A 10-mm diameter glass tube with sintered glass bottom was suspended inside a filtering flask. The sample was placed in the glass tube, nitrogen gas was passed in through the side tube and sintered glass, then bubbled through the sample.

If oxygen removal is complete, the I–Q curve is linear[7] and its slope, K, given by:

$$K = \frac{D\,A}{V\,\delta}$$

where D is the diffusion coefficient, δ is the thickness of the diffusion layer, V is the total volume of solution, and A is the electrode area. If oxygen removal is incomplete, a bend appears in the I–Q curve as in Fig. 9. The reason for the bend is that the diffusion coefficient of oxygen is larger than the diffusion coefficient of copper or lead; consequently, K of oxygen becomes larger than K of copper

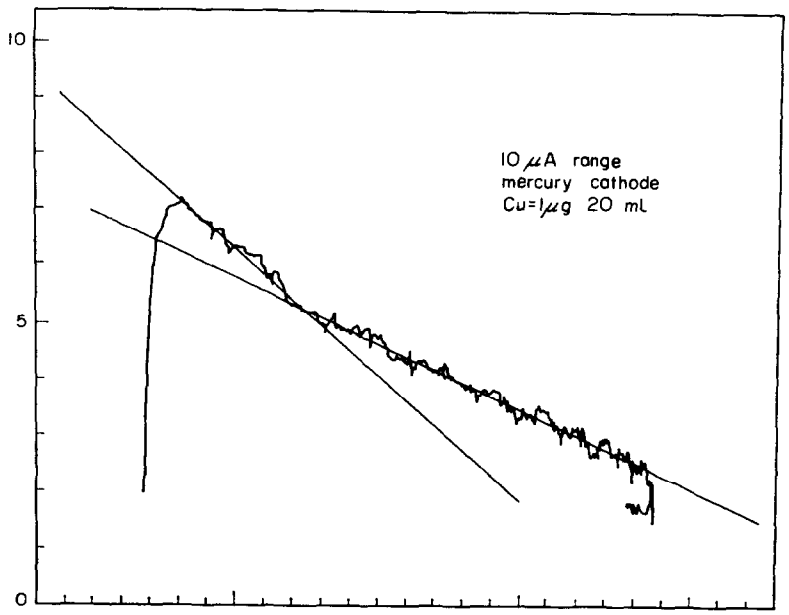


FIG. 9.—Effect of dissolved oxygen.

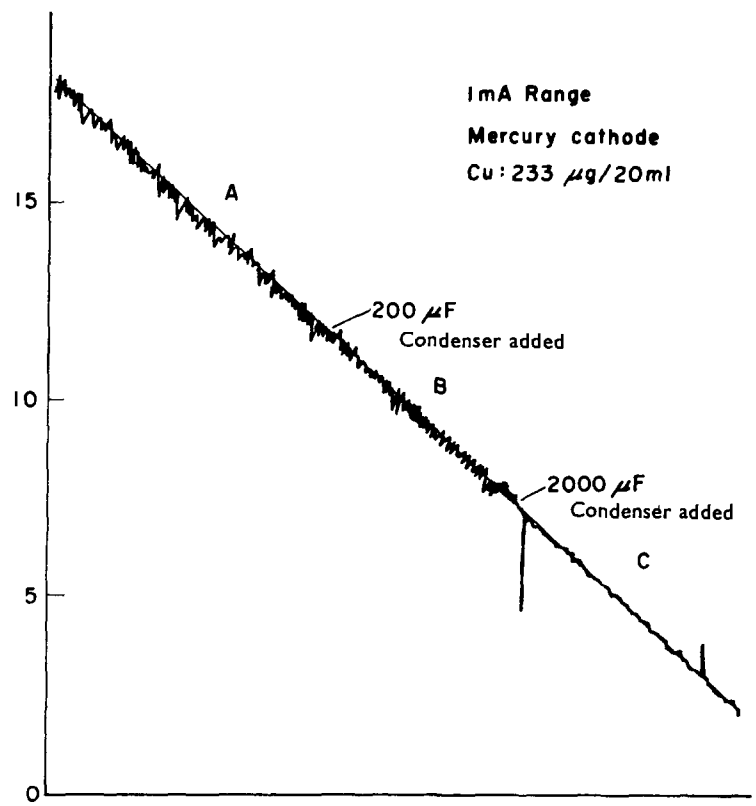


FIG. 10.—Effect of damping circuit.

or lead. Because the effect of oxygen is very great in micro determination, this possibility of checking the oxygen removal from the chart is another advantage of the I–Q recorder.

Damping circuit

Fig. 10 shows the I–Q curve of 233 μg of copper determined at 1-mA range and with mercury cathode; Fig. 12 shows the I–Q curve of 4 μg of lead determined at 10 μA and with mercury cathode. No damping circuit was used when Fig. 12 and the first section of the I–Q curve in Fig. 10 were drawn.

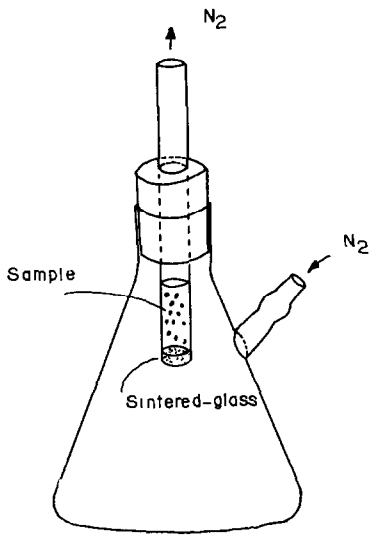


FIG. 11.—Oxygen removal apparatus.

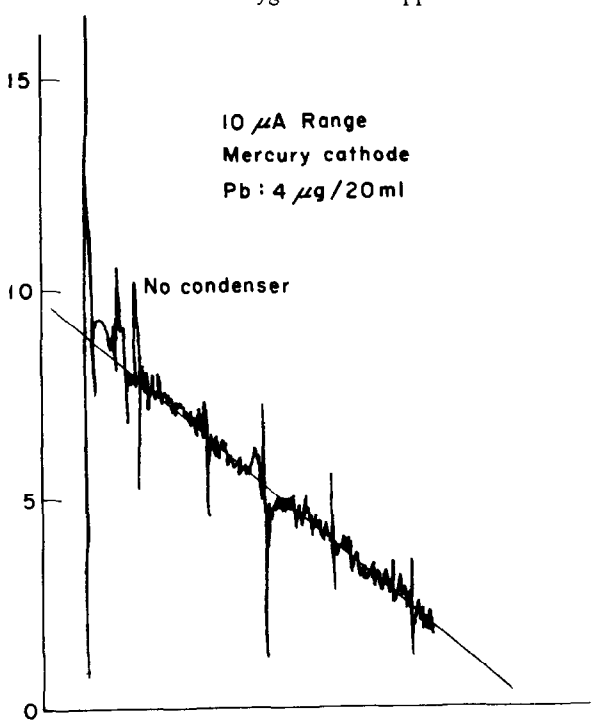


FIG. 12.—I–Q curve with no damping circuit.

In the middle and last sections of Fig. 10, 200-μF and 2000-μF condensers were used, respectively. As the curves show, a damping circuit consisting of a condenser inserted at the terminal of the I–Q recorder is necessary for micro determinations.

The error of the I–Q recorder arising from the addition of the damping circuit is discussed below. The condenser is inserted parallel to the shunt. Because condenser leakage is small in this coulometer, correction is not necessary. Fig. 10 shows the effect of the condenser capacity. Because this I–Q curve remains linear, it can be assumed that the addition of the condenser does not affect the determination. The count/coulomb factor was obtained with and without the condenser, and there was no significance in the factor difference.

Calibration of sampling syringe

To eliminate great change in the 20-ml volume of the electrolyte, a 1·0-ml syringe was used for the 0·5-ml samplings. Another reason for using a syringe was to eliminate oxygen effect. Distilled water was drawn into the syringe and a spacer was inserted between the flanges of the barrel and plunger. The spacer was then removed and the water expelled and weighed. The mean volume was 0·470 ml (standard deviation, 0·001 ml; coefficient of variation, 0·2%).

Electrolysis cell

Fig. 7 shows the electrolysis cell.

Reagents

Copper: A standard solution of copper in the form of $CuSO_4$ was made from 99·99% copper metal.
Lead: The stock solution of lead was made as previously mentioned.

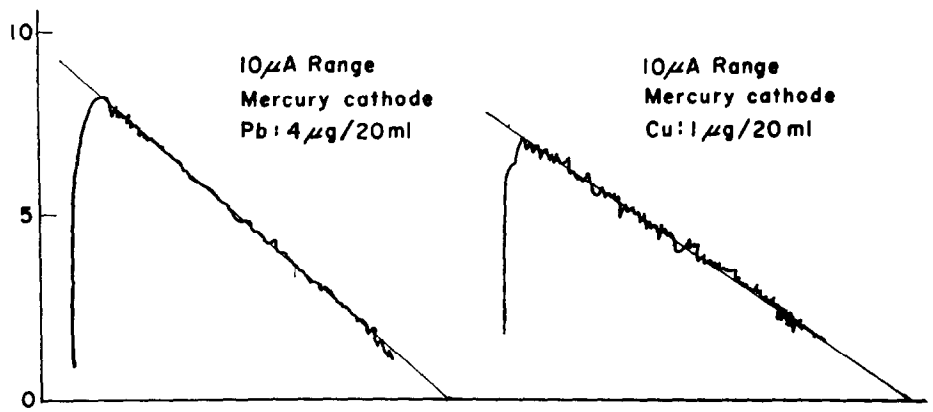


FIG. 13.—I–Q curve for micro determination of lead and copper.

Procedure

Determination of copper: Sample solutions of 2·334 mg/100 ml and 2·33 μg/100 ml were made daily from the stock solution. A sample solution of 2–3 ml was de-oxygenated for at least 1 hr. The electrolysis cell was prepared as above using 0·5*N* hydrochloric acid as supporting electrolyte. The potentiostat was set at −0·34 V *vs.* S.C.E., and the same procedure performed as above. This technique of adding 0·5–1 ml of "dummy" sample solution is particularly important in micro determinations. Equally important is the continual use of nitrogen gas for oxygen removal during determinations. After recording, the chart was constructed, the chart length of Q measured, and the quantity of electricity obtained by multiplying with the factor found from the built-in correction circuit. In this experiment the factor for the 10-μA range was 27·0 mm/millicoulomb and for the 50-μA range 5·36 mm/millicoulomb. The volume of sample measured with the sampling syringe was 0·470 ml and contained 10·97 μg of copper (33·32 millicoulomb) and 1·10 μg of copper (3·33 millicoulomb). The initial current was about 20 μA and 2·5 μA, respectively; the background current was 1·5–3 μA.

Determination of lead: The procedure was the same as that used for copper except that 0·5*M* potassium chloride was used for supporting electrolyte. The potentiostat was set at −0·55 V *vs.* S.C.E. The volume of sample measured with the sampling syringe was 0·470 ml and contained 10·52 μg of lead (9·80 millicoulomb) and 4·21 μg of lead (3·92 millicoulomb). The initial current was about 10 μA and 4 μA, respectively; the background current was 1·5–3 μA.

Figs. 13 and 14 show examples of the I–Q curve of copper and lead when a 2000-μF damping condenser was used.

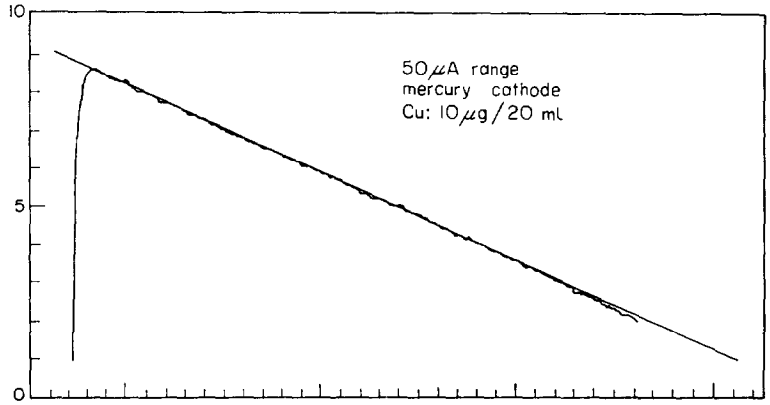


FIG. 14.—I–Q curve for micro determination of copper.

Table VI shows the results of determinations of copper and lead.

The observed values include error introduced during construction of the chart, measurement of the chart length, and other random errors; however, the reproducibility of the determinations is good. When the observed values are compared with the calculated values, the bias is found to be negative and rather large. The results of

TABLE VI.—DETERMINATION OF COPPER AND LEAD

	Sample		Found	Std. dev.	Coeff. var.	Error		Range on meter
	μg	*mcoulombs*	*μg*	*μg*	%	*μg*	%	*μA*
Cu	1·10	3·33	1·01	0·02	2	−0·09	− 9	10
	10·97	33·32	10·78	0·09	0·9	−0·19	− 1·7	50
Pb	4·21	3·92	3·65	0·06	1·7	−0·56	−14	10
	10·52	9·80	10·22	0·07	0·7	−0·3	− 3	10

the experiment show that: (1) The current efficiency seems to be over 100%, but theoretically the current efficiency cannot be over 100%. (2) The I-Q curve is linear in the figure. It can be assumed that there is no side reaction in the electrolysis. (3) Electrical checking proves that this device does not induce these errors. Therefore, it can be assumed that adsorption of the sample on the vessel has a great effect on the determination, because the initial concentration of copper or lead in the electrolyte is very low: $8{\cdot}5 \times 10^{-6}$ and $8{\cdot}5 \times 10^{-7} M$ copper, and $2{\cdot}5 \times 10^{-6}$ and $1 \times 10^{-6} M$ lead.

Acknowledgements—I wish to thank Professor T. Takahashi, Institute of Industrial Science, University of Tokyo, for his valuable suggestions and criticisms during the work. I also wish to thank Professor S. Hirano, Faculty of Engineering, University of Tokyo, for his very helpful advice on many matters and also Mr. M. Katori, Chief Director of the Government Industrial Research Institute, Nagoya, for his keen interest in this work.

Zussammenfassung—Der Autor hat jüngst über die Konstruktion eines direkt ablesbaren Stromintagrators berichtet. Das Gerat wurde jetzt zu einem Schreiber erweitert. Das Diagramm zeigt Integration der Stromkurve längs der X-Achse und irgend ein willkürlich gewähltes Signal längs der Y-Achse. In coulometrischen Analysen zeigt die Kurve

die Elektrizitätsmenge (Q) auf der X und den Elektrolysenstrom (I) auf der Y-Achse. Daher wird das Gerät I–Q Schreiber genannt. Der höchste Empfindlichkeitsbereich ist 10 μA. Die Reproduzierbarkeit ist zu 0·1 % geschätzt. Integration ist möglich zwischen Null und Höchstwert. Die Schnellbestimmung von Mikromengen Kupfer und Blei (1–10 μg, bezw, 4–10 μg) wurde durchgeführt. Die rasche Bestimmung von 0·9 mg Pb und 0·8 mg Cd in deren Mischung wird diskutiert.

Résumé—L'auteur a récemment mis au point un intégrateur de courant à lecture directe avec appareil différentiel, moteur d'intégration, moteur à vitesse constante, tachygénérateur incorporé comme principaux constituants. Après mise au point de l'intégrateur, l'auteur l'a amélioré ultérieurement sous forme d'un enregistreur. Celui-ci donne l'integration du courant le long de l'axe des X et tout signal arbitraire le long de l'axe des Y. Dans une analyse coulométrique, le diagramme donne la quantité d'électricité Q sur l'axe des X et le courant d'électrolyse I sur l'axe des Y. En conséquence l'auteur a appelé son appareil un enregistreur i–Q. Cet enregistreur peut être employé non seulement pour l'analyse coulométrique, mais encore pour d'autres utilisations instrumentales. Le domaine de plus grande sensibilité est 10 μA; la reproductibilité doit être considérée comme étant de 0,1%. L'intégration est possible du zéro jusqu'à la valeur calculée. Un dosage rapide de micro quantités de Cu et Pb, 1–10 μg et 4–10 μg respectivement, a été réalisé en utilisant enregistreur i–Q. Un dosage rapide de 0,9 mg. de Pb et 0,8 mg. de Cd mélangés est aussi discuté.

REFERENCES

[1] J. J. Lingane, *J. Amer. Chem. Soc.*, 1945, **67**, 1916.
[2] *Idem*, *Electroanalytical Chemistry*. Interscience Publishers, New York, 2nd Ed., 1958, p. 452.
[3] J. S. Parsons, W. Seaman and R. M. Amick, *Analyt. Chem.*, 1955, **27**, 1754.
[4] J. J. Lingane and S. L. Jones, *ibid.*, 1950, **22**, 1220.
[5] L. Meites, *ibid.*, 1955, **27**, 1116.
[6] S. Hanamura, *Talanta*, 1959, **3**, 14.
[7] *Idem*, *ibid.*, 1959, **2**, 278.
[8] M. Masui and H. Sayo, *J. Pharm. Soc. Japan*, 1955, **75**, 1515.
[9] T. L. Marple and L. B. Rogers, *Analyt. Chim. Acta*, 1954, **11**, 574.
[10] J. J. Lingane and S. L. Jones, *Analyt. Chem.*, 1950, **22**, 1169.

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QUANTITATIVE TREATMENT OF EXCHANGE EQUILIBRIA INVOLVING COMPLEXANS—I*

GENERAL CONSIDERATION AND SCOPE OF APPLICATIONS IN ANALYTICAL CHEMISTRY

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Summary—For several cases of practical importance in analytical chemistry, the following exchange equilibrium has been considered theoretically:

$$NY + M + nA \rightleftharpoons MY + NA_n$$

In favourable conditions, the determination of a metal M can be substituted by that of a second metal N using various methods including polarography, photometry, solvent extraction, *etc.* Factors influencing such an indirect determination are discussed in detail. Extending the argument, an equation has been proposed to express the colour change in the vicinity of the equivalence point in the chelatometry M using the NY-A system as indicator. It is possible to find the optimum condition for a given problem if the stability constants of the various species involved in the above exchange equilibrium are available.

INTRODUCTION

BY means of an appropriate exchange reaction, it is sometimes possible to substitute for the determination of one metal that of a second metal which can be more easily determined.[1] Again, when it is difficult to find a suitable metal indicator in the chelatometric titration of a metal, it is often possible to apply a visual titration method using, as an indicator, a system containing a second metal forming a more or less stable chelate with the complexan used and a complexing agent giving rise to a sensitive coloration with this metal.[2–5]

The present paper presents a general discussion of the exchange equilibrium involving a complexan, two metals and a complexing agent. The results are given in a form suitable for application to particular problems of which examples will be given in subsequent papers (see also the preceding paper[6]).

GENERAL CONSIDERATION

The following exchange equilibrium (1) involves two metal ions, M and N, a complexan, Y, and another complexing agent, A† (omitting charges for simplicity):

$$NY + M + nA \rightleftharpoons MY + NA_n \qquad (1)$$

* Part I—see ref. 6.

† A represents a co-ordinating species, which could be, for example, NH_3 in ammine complex formation, or 8-quinolinolate ion in 8-quinolinolate formation.

Assuming that there is no complex formation of M with A, the equilibrium constant of (1) is written as follows (assuming activity coefficients of unity):

$$K_1 = \frac{[MY][NA_n]}{[NY][M][A]^n} = \frac{K'_{MY}K_{NA_n}}{K'_{NY}} \qquad (2)^*$$

where K'_{MY} and K'_{NY} denote the *apparent* formation constants of MY and NY respectively and K_{NA_n} the overall formation constant of the species of N–A complexes prevailing under the given condition.

From equation (2)

$$[M] = \frac{[MY][NA_n]}{K_1[NY][A]^n}. \qquad (3)$$

The total analytical concentration of M, N and Y are represented as $[M]_t$, $[N]_t$ and $[Y]_t$, respectively, and are given by equations (4), (5) and (6).

$$[M]_t = [MY] + [M] \qquad (4)$$

$$[N]_t = [NY] + [NA_n] + [N] \qquad (5)$$

$$[Y]_t = [MY] + [NY] + [Y]_t' \qquad (6)$$

If we are concerned with sufficiently large values of K'_{NY} and/or K_{NA_n}, the term [N] in equation (5) may reasonably be neglected. In equation (6), $[Y]_t'$ denoted the total concentration of the complexan not combined with any metal involved. Substituting equation (3) into equation (4), we have

$$[M]_t = [MY]\left(1 + \frac{[NA_n]}{K_1[NY][A]^n}\right). \qquad (7)$$

(*i*) *If* $[N]_t = [Y]_t$

In this case, from equations (5) and (6),

$$[MY] = [NA_n] - [Y]_t'. \qquad (8)$$

In order to take into account the amount of NA_n formed in the following equilibrium:

$$NY + nA \rightleftharpoons NA_n + Y', \qquad (9)\dagger$$

* In the presence of a large excess of a third ligand B, which forms more or less stable complexes with M and N, we should take into consideration the side reaction coefficients β_M, β_N and $\alpha_{H(Y)}$, which are defined as

$$\beta_M = [M]_t'/[M];\ \beta_N = [N]_t'/[N];\ \alpha_{H(Y)} = [Y]_t'/[Y]$$

where $[M]_t'$ and $[N]_t'$ represent the total concentrations of M and N which are combined neither with Y nor with A, and $[Y]_t'$ denotes the total concentration of Y not combined with any metals involved. Then it follows that

$$K_1 = \frac{K_{MY}}{\alpha_{H(Y)} \cdot \beta_M} \cdot \frac{K_{NA_n}}{\beta_N} \cdot \frac{\alpha_{H(Y)} \cdot \beta_N}{K_{NY}} = \frac{K_{MY}K_{NA_n}}{\beta_M K_{NY}} \qquad (2)'$$

where K_{MY} and K_{NY} are the formation constants of MY and NY. In equation (2)′ the following effects are taken into account: protonation of Y, and complex formation of M and N with the ligand B. If M does not form any stable complexes with B, equations (2) and (2)′ become the same, *viz.*,

$$K_1 = \frac{K_{MY}\,K_{NA_n}}{K_{NY}} \qquad (2)''$$

In this paper, the absence of such a ligand is assumed unless otherwise noted, and the expression (2)″ will be used for K_1.

† Even in the absence of M, a certain amount of NA_n is formed by equilibrium (9). This amount is equal to $[Y]_t'$.

Y′ representing all species of uncombined complexan. The equilibrium constant for (9), K_2, is given by equation (10):

$$K_2 = \frac{[NA_n][Y]_t'}{[NY][A]^n} = \frac{K_{NAn}}{K_{NY}} \cdot \alpha_{H(Y)}. \quad (10)$$

From equation (10)

$$[Y]_t' = \frac{[NY]}{[NA_n]} \cdot K_2[A]^n. \quad (11)$$

Combining equations (5), (7), (8) and (11), and solving for $[M]_t$,

$$[M]_t = \left([NA_n] - \frac{[N]_t - [NA_n]}{[NA_n]} \cdot K_2[A]^n\right)\left(1 + \frac{[NA_n]}{[N]_t - [NA_n]} \cdot \frac{1}{K_1[A]^n}\right). \quad (12)$$

Equation (12) is a general expression for $[M]_t$ when $[N]_t = [Y]_t$.

(ii) *If* $[N]_t \neq [Y]_t$

Combining equations (5), (6) and (11), and rearranging,

$$[M]_t = \left\{[Y]_t - ([N]_t - [NA_n]) - \frac{[N]_t - [NA_n]}{[NA_n]} \cdot K_2[A]^n\right\} \times \left\{1 + \frac{[NA_n]}{[N]_t - [NA_n]} \cdot \frac{1}{K_1[A]^n}\right\}. \quad (13)$$

These expressions offer a basis for finding favourable conditions for the indirect determination of M, by the polarography or photometry of an equivalent amount of N, and for the chelatometry of M using a system NY-A as an indicator. These will now be discussed in more detail.

INDIRECT POLAROGRAPHY AND INDIRECT PHOTOMETRY OF NA_n IN AQUEOUS SOLUTION

When M is to be determined indirectly by the polarography or photometry of NA_n in aqueous solution, using the exchange reaction (1), a very favourable, though not necessarily an indispensible condition is:

$$[M]_t = [NA_n]. \quad (14)$$

Equation (14) holds provided that

(*a*) $K_2[A]^n$ is sufficiently small in equation (12); in other words, that $[Y]_t'$ can be neglected in equation (8), and

(*b*) the term $\frac{[NA_n]}{[N]_t - [NA_n]} \cdot \frac{1}{K_1[A]^n}$ is much smaller than unity in equation (12).

If condition (*a*) is satisfied, equation (12) simplifies to

$$[M]_t = [NA_n]\left(1 + \frac{[NA_n]}{[N]_t - [NA_n]} \cdot \frac{1}{K_1[A]^n}\right). \quad (15)$$

From a practical point of view, it may be assumed that equation (14) holds if the second term in the parenthesis of equation (15) is smaller than 10^{-2}. In Table I, the ranges of $[M]_t/[N]_t$ where equation (14) holds for different values of $K_1[A]^n$ are given.

This shows that the greater the value of $K_1[A]^n$, the wider is the range of $[M]_t/[N]_t$ where equation (14) holds. If K_1 is the equilibrium constant for expression (1), given

by $K_{MY}K_{NA_n}/K_{NY}$,* it is possible to find a favourable value of K_1 for the determination of M by a reasonable choice of metal N, complexan Y and complexing agent A, *viz.* by an appropriate combination of K_{MY}, K_{NY}, K_{NA_n}. Even after choosing N, Y and A, [A] may be varied to obtain a desirable large value for $K_1[A]^n$. However, it should be noted that since the relationship $K_1/K_2 = K'_{MY}$ always holds, the value of K'_{MY} must be reasonably high to produce a sufficiently high value of K_1 together with a sufficiently low value of K_2.

TABLE I.—RANGES OF $[M]_t/[N]_t$ WHERE EQUATION (14) OR EQUATION (19) HOLDS

$K_1[A]^n$ or $K_3[A]^n$	$[M]_t/[N]_t$
10^4	<0.99
10^3	<0.90
10^2	<0.50

INDIRECT DETERMINATION OF M BY MEANS OF SOLVENT EXTRACTION OF NA_n

To discuss the distribution of the species NA_n between aqueous and organic phases, we consider equation (16):

$$(NY)_w + (M)_w + n(A)_w \rightleftharpoons (NA_n)_0 + (MY)_w, \tag{16}$$

where the subscripts *w* and *o* refer to the aqueous and organic phases, respectively. The equilibrium constant for (16), K_3, may be written as follows:

$$K_3 = \frac{[NA_n]_o[MY]_w}{[NY]_w[M]_w[A]_w^n} = \frac{K_{MY}K_{NAn}}{K_{NY}} \cdot K_D, \tag{17}$$

where K_D refers to the distribution coefficient of NA_n between the aqueous and organic phases. In much the same way as in the preceding section, we obtain

$$[M]_t = [NA_n]_o \left\{1 + \frac{[NA_n]_o}{[N]_t - [NA_n]_o} \cdot \frac{1}{K_3[A]_w^n}\right\}. \tag{18}$$

Equation (18) is quite similar to equation (15). As already mentioned, the higher the value of $K_3[A]_w^n$, the wider is the range of $[M]_t/[N]_t$ where the equation (19) holds (see Table I):

$$[M]_t = [NA_n]_o \tag{19}$$

Now values such as K_D, K_{NA_n}, *etc.*, are not usually known separately. On the other hand, when HA, a weak acid, is used as reagent in the solvent extraction of N, the following relationship is known to hold,[7] as long as the concentration of HA in the organic phase, $[HA]_o$, remains constant:

$$\log D = n(pH - pH_{1/2}) \tag{20}$$

So it might be more convenient to relate $K_3[A]_w^n$ to the pH at the half extraction of N (designated as $pH_{1/2}$) and the pH of the aqueous phase concerned, both of which can be directly determined experimentally.

From the definition of K_D and equation (17)

$$K_3[A]_w^n = \frac{K_{MY}}{K_{NY}} \cdot \frac{[NA_n]_o}{[N]_w}. \tag{21}$$

And if it is assumed that any complexation other than that of NA_n is not appreciable,

* In the presence of a third ligand B, these constants must be apparent ones.

$[NA_n]_o/[N]_w$ may be regarded as the distribution ratio of N (designated as D) between the two phases. Thus

$$D = \frac{[NA_n]_o}{[N]_w}. \tag{22}$$

Combining equations (20), (21) and (22)

$$\log K_3[A]_w^n = \log K_{MY} - \log K_{NY} + n(pH - pH_{1/2}). \tag{23}$$

As seen from equation (23), the values of $K_3[A]_w^n$ is determined by a choice of M, N, Y, HA, $[HA]_t$ and the pH at which the extraction is carried out. Therefore by an appropriate choice of these, it is possible to find favourable conditions for the given problem.

CHELATOMETRIC TITRATION OF M USING A SYSTEM NY-A AS INDICATOR

When M is to be determined chelatometrically using a system NY-A as indicator, the condition $[M]_t \gg [NA_n]$ is necessary.* To realise this condition, either of the following two conditions should be satisfied:

(*i*) $[M]_t \gg [N]_t$,
(*ii*) $[M]_t \gg [A]_t$.

We can reasonably confine ourselves to the consideration of the colour change in the vicinity of the equivalence point in these two cases.

(*i*) $[M]_t \gg [N]_t$.

In this case, $[N]_t$ being very small, N should not necessarily be added as NY. However, $[A]_t$ should not be too great when we are concerned with a strongly coloured free indicator or a sparingly soluble one. Accordingly, the consideration of this case is especially useful when one uses a colourless indicator belonging to the first group in the classification[8] by Körbl and Přibil.

Designating the total concentration of complexan used in the titration as $[Y]_t''$, it may be assumed that in the vicinity of the equivalence point $[Y]_t \gg [N]_t$ and $[Y]_t \fallingdotseq [Y]_t'' \fallingdotseq [M]_t$.

Thus neglecting $[N]_t - [NA_n]$ as compared with $[Y]_t$ in equation (13),

$$[Y]_t''/[M]_t = 1 - \frac{[NA_n]}{[N]_t - [NA_n]} \cdot \frac{1}{K_1[A]^n} + \frac{[N]_t - [NA_n]}{[NA_n]} \cdot \frac{K_2[A]^n}{[M]_t} + \frac{1}{K'_{MY}[M]_t}. \tag{24}$$

The last term in equation (24) may reasonably be neglected under the ordinary condition of chelatometry, though it becomes significant in the titration of a very dilute solution, in the case of small K'_{MY}, or at a point very close to the equivalence point.† Thus neglecting the last term

$$[Y]_t''/[M]_t = 1 - \frac{[NA_n]}{[N]_t - [NA_n]} \cdot \frac{1}{K_1[A]^n} + \frac{[N]_t - [NA_n]}{[NA_n]} \cdot \frac{K_2[A]^n}{[M]_t} \tag{25}$$

Equation (25) is an expression relating $[NA_n]$ to $[Y]_t''/[M]_t$ in the chelatometry of M with Y. The second term is principally concerned with the colour change before

* $[NA_n]$ should be reasonably small. To achieve a sensitive colour change with a small $[NA_n]$, the molar extinction coefficient of NA_n should be reasonably large.

† If $K'_{MY} > 10^8$, this term can be neglected except between 100·000% and 100·001% titration of a $10^{-3}M$ solution of M.

the equivalence point, and the third is principally concerned with that after the equivalence point. To achieve a sharp colour change at the equivalence point, the titration should be carried out under conditions where there is a sufficiently large value of K_1 and a sufficiently small value of K_2. If the numerical values of K_1, K_2, [A] and $[M]_t$ are all available, we can determine the colour change in the vicinity of the equivalence point, plotting $[NA_n]/[N]_t$ against $[Y]_t''/[M]_t$. As indicated earlier, K_1 and K_2 being values determined by M, N, Y and A, we can select N, Y and A to obtain favourable values of K_1 and K_2. However it should be noted that there always

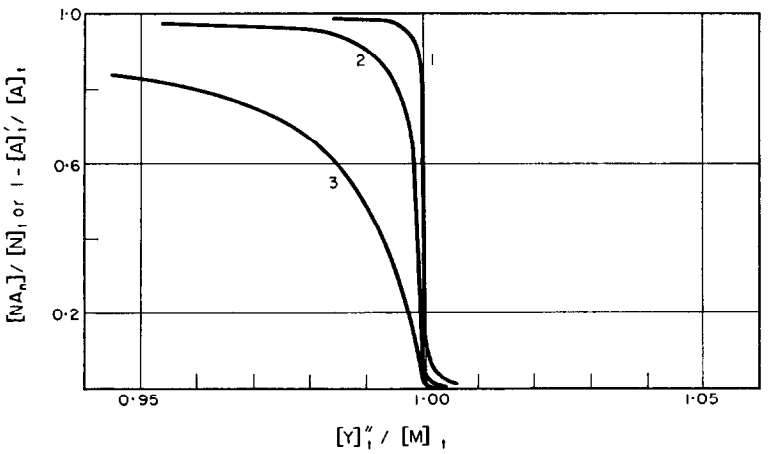


FIG. 1.—Colour change in the vicinity of the equivalence point in the chelatometry of M, using the NY-A system as indicator.

$[M]_t = 10^{-3}M$, $K_{MY} = 10^{11}$
Curve 1: $p = 10^4$, $q = 10^{-7}$;
Curve 2: $p = 10^3$, $q = 10^{-8}$;
Curve 3: $p = 10^2$, $q = 10^{-9}$.

[p and q represent $K_1[A]^n$ and $K_2[A]^n$ respectively in the case (*i*) $[M]_t \gg [N]_t$, and $K_1[NY]/\alpha_{H(A)}$ and $K_2[NY]/\alpha_{H(A)}$ respectively in the case (*ii*) $[M]_t \gg [A]_t$. It is assumed that there is no volume change in the course of the titration.]

exists the relation $K_1/K_2 = K'_{MY}$ between K_1 and K_2. Because $K'_{MY} = K_{MY}/\alpha_{H(Y)}\beta_M$, we are able to predict the possible pH range for the titration and the permissable concentration of the third ligand. For the case where $K'_{MY} = 10^{11}$ (*e.g.*, $K_{Ca\text{-}EDTA} = 10^{10.8}$) and $[M]_t = 10^{-3}$M, Fig. 1 shows the plot of $[NA_n]/[N]_t$ against $[Y]_t''/[M]_t$ for various couples of $K_1[A]^n$ and $K_2[A]^n$. Analogous figures can be drawn for each case, and will be useful to predict a favourable condition for a specific problem.

(*ii*) $[M]_t \gg [A]_t$.

This is the particular case of a chelatometric titration using a proper metallochromic indicator.[8]

Neglecting [N] in equation (5), from equations (5) and (13)

$$[M]_t = \left([Y]_t - [NY] - \frac{[A]^n}{[NA_n]} \cdot K_2[NY]\right)\left(1 + \frac{[NA_n]}{[A]^n} \cdot \frac{1}{K_1[NY]}\right). \qquad (26)$$

Assuming that N is added as NY, which is reasonably stable in the prevailing conditions, $[Y]_t - [NY]$ is the total concentration of the complexan used in the course of titration. This amount is represented as $[Y]_t''$, as in the preceding section. In the

vicinity of the equivalence point, $[M]_t \fallingdotseq [Y]_t''$. Thus, neglecting the last term as before

$$[Y]_t''/[M]_t = 1 - \frac{[NA_n]}{[A]^n} \cdot \frac{1}{K_1[NY]} + \frac{[A]^n}{[NA_n]} \cdot \frac{K_2[NY]}{[M]_t}. \quad (27)$$

Assuming that A does not form any complexes other than the 1:1 complex NA,*

$$[Y]_t''/[M]_t = 1 - \frac{[NA]}{[A]_t'} \cdot \frac{\alpha_{H(A)}}{K_1[NY]} + \frac{[A]_t'}{[NA]} \cdot \frac{K_2[NY]}{\alpha_{H(A)}[M]_t} \quad (28)\dagger$$

where $\alpha_{H(A)} = [A]_t'/[A]$ and $[A]_t'$ denoted the total concentration of A not combined with N. In the titration of M we can find favourable values of K_1 and K_2 by an appropriate choice of N, Y, and A. Moreover for a certain set of K_1 and K_2, [NY] and pH are important factors in deciding the experimental procedure for a given problem (see Fig. 1).‡

Zusammenfassung—Das folgende Austauschgleichgewicht ist in verschiedenen analytischen Problemen von praktischer Bedeutung und wurde theoretisch behandelt;

$$NY + M + nA \rightleftharpoons MY + NA_n$$

Unter günstigen Bednigungen kann die Bestimmung des Metalles M durch die eines zweiten Metalles N ersetzt werden wie z.B. in polarographischen, spektrophotometrischen, extraktiven und anderen Bestimmungsverfahren. Die Faktoren, welche solch eine Bestimmung beeinflussen werden im Detail studiert. Eine Formel wird abgeleitet, die es gestattet den Farbwechsel im Bereich des Aquivalenzpunktes von chelatometrischen Titrationen zu bestimmen wenn M titriert und das System NY-A als Indicator verwendet wird. Die Ergebnisse der vorliegenden theoretischen Untersuchungen gestatten die Berechnung der optimalen Bedingungen, vorausgesetzt die Stabilittäskonstanten der verschiedenen Komplexe sind bekannt.

Résumé—En raison de son importance pratique en chimie analytique la réaction d'échange:

$$NY + M + nA \rightleftharpoons MY + NA_n$$

a été étudié au point de vue théorique. Lorsque les conditions sont favorables le dosage d'un métal M peut être remplacé par celui d'un second métal N en utilisant des méthodes variées comme la polarographie, la spectrophotométrie, l'extraction, etc.

Les facteurs qui influencent une telle détermination indirecte sont discutés en détail. Une équation est proposée qui exprime le changement de coloration au voisinage du point équivalent dans le dosage complexométrique de M en utilisant le système NY-A comme indicateur. A partir des résultats obtenus, il est possible de déterminer les conditions optimales pour un problème donné, dans la mesure où l'on connait les constantes de stabilité des différentes espèces chimiques mises en jeu dans la réaction d'échange considérée.

* In chelatometry, using MgY-Erio T system as indicator, a 1:1 complex is known to be formed. In cases where higher complexes have to be taken into consideration, $[A]_t'$ affects the colour change and equation (28) becomes more complicated. A quantitative treatment of these cases will be published in near future.

† $[A]_t' = [A] + [HA] + [H_2A] + \cdots + [H_jA]$. The colour of the dissociated form A often resembling that of NA, another indicator or condition is preferably to be sought, if [A] can not be neglected.

‡ Where there is also present a third ligand, which forms a reasonably stable complex with N but not with M, its influence appears in the diminution of [NY], of which the degree is dependent on the value of $[Y]_t''/[M]_t$, and hence the colour change becomes obscure [*cf.* equations (2)′ and (28)].

REFERENCES

[1] R. Přibil and E. Vicenová, *Coll. Czech. Chem. Comm.*, 1953, **18,** 308.
[2] G. Schwarzenbach, *Die komplexometrische Titration.* Dritte Auflage, Ferdinand Enke Verlag, Stuttgart, Germany, 1957, p. 60.
[3] A. Ringbom, G. Pensar and E. Wänninen, *Analyt. Chim. Acta*, 1958, **19,** 525.
[4] F. S. Sadek, R. W. Schmid and C. N. Reilley, *Talanta*, 1959, **2,** 38.
[5] E. Wänninen, *ibid.*, 1961, **8,** 355.
[6] Genkichi Nakagawa and Motoharu Tanaka, *ibid.*, 1962. **9,** 847.
[7] G. H. Morrison and H. Freiser, *Solvent Extraction in Analytical Chemistry.* John Wiley and Sons Inc., New York, U.S.A., 1957, p. 55.
[8] J. Körbl and R. Přibil, *Coll. Czech. Chem. Comm.*, 1957, **22,** 1122.

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THE POLAROGRAPHY OF SILVER

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Summary—A true polarographic wave for silver may be obtained in a cyanide medium from which the excess of unreacted cyanide ion is removed by addition of excess of nickel ions. None of the common anions interferes, even thiosulphate, nor do any of the metals examined except Tl^+. The coincident wave of Pb^{2+} may be removed to more cathodic potentials by addition of excess of ethylenediaminetetra-acetic acid.

SINCE silver is more noble than mercury, especially in dilute amalgams, and since both metals form complexes of similar stabilities with the same ligands, it is usually impossible to determine the true half-wave potential of silver ion or its complexes at a dropping mercury electrode. The true reduction potential of silver from most supporting electrolytes is more positive than the potential at which anodic dissolution of mercury begins, and consequently it is only possible to observe a diffusion current due to silver ion and it is practically impossible to observe a full polarographic wave. This type of analytical method has been used in an alkali nitrate or perchlorate medium. The diffusion current under these conditions and with a mercury pool anode is observed at zero applied potential.

Consequently, in order to obtain a fully defined silver wave a complexing agent must be used which forms a more stable complex with silver ions than with mercury^{I} or mercury^{II} ions and which thus shifts the reduction potential of the silver ion to a more negative potential than the mercury wave. An examination of the literature relating to stability constants reveals that few such accessible ligands exist and consequently an alternative procedure must be found.

In our preliminary experiments we examined several common inorganic ligands well known to form powerful complexes with silver ion, *e.g.*, iodide [AgI_4^{3-}, $\beta_4 \approx 15$], thiosulphate [$Ag_2(S_2O_3)_2^{2-}$, $\beta_2 \approx 13$], thiocyanate [$Ag(SCN)_4^{3-}$, $\beta_4 \approx 11$] and cyanide [$Ag(CN)_2^-$, $\beta_2 \approx 21$]. All four ligands form somewhat more stable complexes with mercury ions than they do with silver, however. It is therefore necessary to remove the excess of the complexing agent from the silver solution before carrying out polarography. Thus it has previously been shown that it is possible to obtain a well defined silver wave at the dropping mercury cathode when a pure solution of potassium argentocyanide is used.[1] Unfortunately, whilst this is of academic interest it does not furnish a practicable method for the analysis of dilute silver solutions by polarography.

We therefore examined three main possibilities for the removal of excess of complexing agents. The first of these was based on removal by shaking with an excess of insoluble substance which will remove complexing agent without breaking down the silver complex. Thus for iodide ion, with mercuric oxide, the appropriate reaction is:

$$4I^- + HgO + H_2O \rightleftharpoons HgI_4^{2-} + 2OH^-$$

The second method involved addition of another metal ion capable of binding the excess of complexing agent in a soluble complex without breaking down the silver complex. Thus nickel ion may be used to remove an excess of cyanide ion:

$$4CN^- + Ni^{2+} \rightleftharpoons Ni(CN)_4^{2-} \quad (\beta_4 \approx 16)$$

The third method involved destruction of the excess of complexing agent or binding it in a non-reactive form. Thus cyanide ion can be bound as cyanhydrin, since the product formed,

$$H^+ + CN^- + HCHO \rightarrow H_2C\begin{matrix}OH\\ \diagup\\ \\ \diagdown\\ CN\end{matrix},$$

is not reducible at the dropping mercury electrode.

It was found that the first method was not successful because the equilibrium was attained before removal of all the complexing agent. When the method was used on a continuous-removal basis (*i.e.*, in column form) reaction also took place with the silver complexes. Accordingly, attention was restricted to the second and third methods. The latter method is most easily applied to cyanide ion, which is one of the most powerful complex formers for silver ion.

A $10^{-3}M$ potassium cyanide solution in a $10^{-1}M$ potassium nitrate base electrolyte was found to give an anodic wave for the cyanide ion at $-0{\cdot}45$V against a calomel element immersed in $10^{-1}M$ KNO_3 and connected to the solution *via* a bridge containing the same electrolyte. When silver was added to a similar solution in amount sufficient to leave a slight excess of free cyanide ion, the polarogram showed a half-wave potential at $-0{\cdot}55$V, with a pronounced maximum at *ca.* $-0{\cdot}75$V. The maximum was readily removed by the addition of a suppressor such as methyl red The wave obtained in its presence was typically cathodic in form and the diffusion current was considerably greater than in the presence of cyanide ion alone. However, these experiments demonstrate the lack of sufficient separation between the waves even under favourable conditions and the necessity for removal of the excess cyanide is apparent. It was found, however, that when the above experiment was repeated in the presence of an excess of formaldehyde, whilst the wave from free cyanide could be removed completely, so also could the wave from the silver-cyanide complex. No waves whatsoever were obtained.

Attention was now given to the possibility of applying the second method previously mentioned and here again the silver complex with cyanide ion was used. Many metals form stable cyanide complexes, but a consideration of the stability constants involved reveals that for general applicability of the method, particularly for the determination of silver in the presence of other heavy metals, nickel ion should serve best.

When increasing amounts of nickel solution were added to a $2 \times 10^{-4}M$ KCN solution, $10^{-1}M$ with respect to KNO_3, it was observed that the cyanide wave measured as described previously against the same reference electrode was progressively reduced till it eventually disappeared. Waves caused by excess nickel appeared at $E_{\frac{1}{2}}$ *ca.* $-1{\cdot}1$V and by $Ni(CN)_4^{2-}$ at $E_{\frac{1}{2}}$ *ca.* $-1{\cdot}4$V.

When nickel was added similarly to silver solutions containing an excess of cyanide

ion, it was found that the silver-cyanide complex was not broken up and a true polarographic wave from the $Ag(CN)_2^-$ ion was obtained at $E_{\frac{1}{2}} = -0{\cdot}50V$ against the electrode previously described* *cf.* Fig. 1. A plot of $\log_{10}\frac{id - i}{i}$ against V gave an "n" value of 0·98, indicating a one electron transfer at the electrode.

The analytical utility of the wave was investigated and confirmed for silver concentrations within the range $10^{-4} - 10^{-6}M$. In some respects with $\leqslant 10^{-5}M$ solutions it was found more convenient for quantitative purposes to omit the Ni^{2+} solution and to correct the diffusion current for the small current observed with a cyanide "blank" solution at the same voltage. This was because the effect of adding nickel at the higher instrument sensitivities used for *ca.* $10^{-6}M$ Ag^+ solutions greatly increased the residual current.

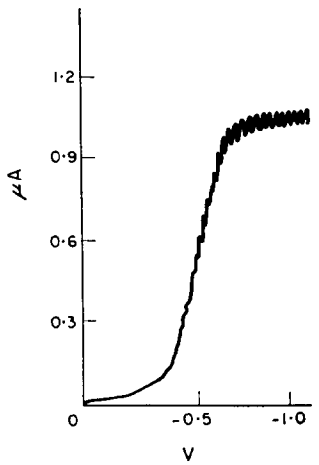


FIG. 1.—Polarogram of silver ions in the presence of excess KCN and $NiSO_4$.

Interferences. The interference of the following ions was determined: Co, Fe^{II}, Fe^{III}, Cu,^{II} Ni, Zn, Cd, Pb, Tl^I, Bi, Th and Al. These tests were carried out with a two-fold excess of these ions on a solution $5 \times 10^{-5}M$ in silver ion, $2 \times 10^{-4}M$ in KCN, $10^{-1}M$ in KNO_3 and 10^{-5}% with respect to methyl red, with and without added nickel sulphate as described above. The following did not interfere with the $Ag(CN)_2^-$ wave, but produced waves of the indicated $E_{\frac{1}{2}}$ values: Co (−1·4V), Zn (−1·35V), Cd (−0·9V) and Fe^{II} (−1·6V). By adjusting the pH of the solution to *ca.* 6·5 the following also did not interfere: Al (−2·0V), Bi (−0·15V) and Th (no wave).

Pb (−0·6V) and Tl^I (−0·5V) interfered by yielding waves at the same potentials as the silver complex. The interference of lead was overcome by addition of an excess of EDTA and careful buffering to pH 6·5–7·0. This moved the lead wave along to *ca.* −1·4V without affecting the silver wave. This method cannot, however, be applied for Tl because the latter does not form a stable EDTA complex. The interference of Tl^I could most probably be overcome by oxidation to Tl^{III}, but no further examination was made of this aspect.

Fe^{III} and Cu^{II} interfered by forming strong cyanide complexes and consuming

* Measured against a dip-type calomel cell (E.I.L. Type RJ/23) immersed directly in the test solution, the value of $E_{\frac{1}{2}}$ was −0·26 to −0·28 V, S.C.E.

cyanide ion, but their interference was readily circumvented by adding a sufficient excess of cyanide ion to complex the silver and also the interfering ion, followed by an excess of nickel sulphate to remove the free cyanide. In this instance a complete polarogram in the cathodic area still reveals only the wave from $Ag(CN)_2^{2-}$, free Ni^{2+} and $Ni(CN)_4^{2-}$, since the cupricyanide complex originally formed quickly reverts to cuprocyanide *via* the reaction

$$2Cu(CN)_4^{2-} \rightleftharpoons 2Cu(CN)_3^{2-} + C_2N_2,$$

and the latter does not yield a polarographic wave in this medium. The same behaviour is observed with Fe^{III}, since ferricyanide is reduced at positive potentials with a dropping mercury cathode.

No extensive examination was made of the effect of anions, since the $Ag(CN)_2^-$ complex is much stronger than most other silver-anion complexes, but thiosulphate was selected as the most probable interference. However, under the recommended conditions no interference was observed from its reduction wave at $-0{\cdot}2$V even when a ten-fold amount was present.

DISCUSSION

A procedure has been devised for the determination of silver based on the well defined reduction wave formed by its cyanide complex. The wave occurs at a potential at which very few other metal ions or their cyanide complexes are reduced, but procedures have been devised for the removal of interference by lead, copper and iron^{III}. Thallium^{I} is the only common cation still to interfere amongst those examined by us. Even strongly complexing anions such as thiosulphate do not interfere with the recommended procedure.

We have been unable to reproduce the wave previously reported by other workers for silver in a fluoride medium.[2] To the best of our knowledge the procedure recommended here is the only one that can be applied to obtain a completely defined polarogram for silver ion in dilute solution. Other procedures appear only to offer a diffusion current arising from the presence of silver ion in the solution.

EXPERIMENTAL

Apparatus

(a) Tinsley Mark 17 Recording Polarograph.

(b) Calomel Cell (Electronic Instruments Ltd. RJ/23) with $10^{-1}M$ KNO_3 electrolyte in place of saturated KCl solution. This was connected to the cell *via* a $10^{-1}M$ KNO_3 bridge.

Reagents

$10^{-3}M$ $AgNO_3$, $10^{-2}M$ KCN, $1M$ KNO_3, $10^{-2}M$ $NiSO_4{\cdot}8H_2O$, 0·01% methyl red, 20% ammonium acetate.

Procedure

Pipette $\leqslant$10-ml aliquots of $10^{-3}M$ $AgNO_3$ solution into 100-ml standard flasks together with 2 ml of $10^{-2}M$ KCN and 1 ml of $10^{-2}M$ Ni^{2+} solution. Add 10 ml of $1M$ KNO_3 as base electrolyte and 0·1 ml of 0·01% methyl red as maximum suppressor. Dilute to 100 ml with distilled water. Deoxygenate a sample of this solution in the polarographic cell by passing hydrogen through it for *ca.* 10 min, and obtain a polarogram over the range $-0{\cdot}3$ to $-0{\cdot}8$ V. (A drop time of 3 sec against a head of 35 cm of Hg was employed in this work at a sensitivity of 1·5 μA full scale deflection. The temperature was 18° and 2 units of damping were employed).

Silver in presence of Cu^{2+}

The following procedure may be applied for up to 0·6 mg of Cu^{2+} in the presence of $\leqslant$10 ml of $10^{-3}M$ Ag^+.

Proceed as described above, but add 7 ml of $10^{-2}M$ KCN followed by 2 ml of $5 \times 10^{-2}M$ Ni^{2+}, 10 ml of $1M$ KNO_3 and 0·1 ml of 0·01% methyl red. Proceed from this point as before.

Silver in presence of Pb^{2+}

The following procedure may be applied for up to 2 mg of Pb^{2+} in presence of $\leqslant$10 ml of $10^{-3}M$ Ag^+.

Follow the standard procedure, but after addition of the Ni^{2+} solution add 1 ml of $10^{-2}M$ EDTA and sufficient 20% ammonium acetate solution to restore the pH to 6·5–7·0, followed by 10 ml of $1M$ KNO_3 and methyl red. From this point follow the normal procedure.

Note: The two variations of the normal procedure should be capable of extension to deal with much larger amounts of Cu^{2+} and Pb^{2+} ions. The standard procedure may also be reproduced with aliquots of $10^{-4}M$ Ag^+ solutions which are subsequently diluted to 100 ml, using in this case $10^{-3}M$ KCN and $10^{-3}M$ $NiSO_4$, generally omitting the Ni^{2+} solution, and correcting for the small current from the cyanide ion, as measured on a separate solution not containing any silver ion. The nickel solution need only be added when dealing with interfering ions such as Cu^{2+} and Fe^{3+}.

Zusammenfassung—Eine wahre polarographische Welle für Silber in Cyanidelösung kann erhalten werden, wenn überschüssiges Cyanide mit Nickel abgebunden wird. Keines der gewöhnlichen Anionen stört, auch nicht Thiosulfat und von den Metallen, soweit untersucht, wurde nur Thallium(I) als störend gefunden. Die Koinzidenz der Bleiwelle kann durch zugabe von ÄDTE behoben werden.

Résumé—Une vague polarographique de l'argent peut être obtenue en milieu cyanure en éliminant l'excès de cyanure par addition d'un excès d'ions nickel. Les anions courants ne gênent pas, même les thiosulfates, et il en est de même des métaux étudiés, à l'exception de Tl^+. La vague due à Pb^{2+}, qui se superpose à celle de l'argent, peut être déplacée vers des potentiels plus négatifs par l'addition d'un excès d'acide éthylènediaminetétracétique.

REFERENCES

[1] E. B. Sanigar, *Rec. trav. chim.*, 1925, **44**, 549.
[2] P. W. West, J. Dean and E. J. Breda, *Coll. Czech. Chem. Comm.*, 1948, **13**, 1.

Talanta, 1962, Vol. 9, pp. 931 to 938. Pergamon Press Ltd. Printed in Northern Ireland

DETECTION AND ESTIMATION OF SOME POLYNUCLEAR HYDROCARBONS BY ELECTRON SPIN RESONANCE

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Summary—Certain polynuclear hydrocarbons are quantitatively converted into the free radical form on the surface of a strongly dehydrated silica-alumina catalyst. The resulting radical species are stable in the adsorbed state and their detection and estimation by electron spin resonance technique is described. Less than 10^{-10} mole of hydrocarbon can be detected. The application of this technique to the estimation of anthracene, perylene, dimethylanthracene and naphthacene is described.

INTRODUCTION

ALTHOUGH the high sensitivity of electron spin resonance technique makes it potentially attractive as an analytical tool, its application in analysis has so far been strictly limited. This is in contrast to the closely related phenomenon of nuclear magnetic resonance which has already demonstrated its importance in a wide field of analytical and structural applications.[1] The explanation for this difference lies partly in the unfamiliarity of microwave experimental technique and to a greater extent, so far as free radicals are concerned, in the short-lived nature of the species under investigation. The method is, of course, applicable only to elements or compounds possessing an unpaired electron or which can readily be converted into a free radical form. For species possessing an uncoupled electron-spin the theoretical limit of sensitivity approaches 10^9 radicals, while realisable sensitivities at room temperature with currently available commercial instruments approach 10^{11} uncoupled spins, or less than 10^{-12} mole.

Recently, Rooney and Pink[2] and Brouwer[3] have shown that certain polynuclear hydrocarbons are converted readily into a free radical form by electron transfer at the surface of a freshly activated silica-alumina catalyst. The apparently quantitative nature of the conversion with anthracene and the stability of the radical ions formed on the catalyst surface suggested that this novel reaction might have analytical implications. The present paper describes the application of the technique to the detection and estimation of a number of hydrocarbons.

EXPERIMENTAL

Apparatus

Electron spin resonance measurements: Electron spin resonance (ESR) spectra were obtained at room temperature with a conventional transmission spectrometer operating at 9370 Mc/sec and a magnetic field modulated at 100 kc/sec.[4] The instrument stability was such that at the amplifier gain settings used in analysis base-line drift amounted to less than 3% of full-scale deflection of the recorder over a period of several hr. Low-temperature dextrose-charcoal samples, with free radical concentrations in the range 10^{16}–10^{18} spins, were used as a check on amplifier gain and stability throughout the course of an analytical determination. The amplifier stability was such that the signal amplitude (peak to peak height on the first derivative curve) for the charcoal samples changed by less than 4% over a period of 3 hr after initial warm-up. The sensitivity of the spectrometer for hydrocarbon radicals was about 10^{14} uncoupled electron-spins, corresponding to $\sim 10^{-10}$ mole.

Sample tubes: Samples were contained in 6-mm glass tubes which were carefully selected to be of uniform bore and volume by direct comparison in the spectrometer using a benzene solution of 1,1-diphenyl-2-picrylhydrazyl (DPPH) as standard. Tubes giving a signal amplitude which differed by more than 2% from the mean value were rejected.

The intensity of the signal from a given radical sample was found to be a function of the specimen depth in the microwave cavity. However, when the length of active sample lay within the range 19–22 mm the ESR signal intensity was unchanged. In all quantitative experiments the depth of sample was kept within this range.

Reagents

Catalyst: The silica-alumina catalyst was a commercial sample supplied by Imperial Chemical Industries Limited (Billingham Division) in pellet form (composition: Al_2O_3, 10%; Fe_2O_3, 0.05–0·10%; SiO_2, 89·7–89·9%). Its surface area measured by nitrogen adsorption was about 250 m^2/g. The pellets were crushed, sieved to 60 mesh B.S.S., and activated in air by heating to approximately 600° for a period of 2 hr. 44–60 mesh catalyst was chosen following a series of experiments in which this size of particle was found most convenient to handle in the analytical procedure described later. Activated catalyst was stored over phosphoric oxide in a desiccator. It gave no detectable ESR absorption. On exposure to the atmosphere it gradually lost activity through absorption of moisture. However, provided the catalyst was used in solutions well below its saturation capacity, brief exposure to the atmosphere was found to interfere in no way with the analytical results.

Solvents: AnalaR carbon disulphide and benzene were stored over active silica-alumina catalyst nd filtered befo re use. No further purification appeared necessary.

Polynuclear hydrocarbons: The anthracene used was Hopkin and Williams' micro-analytical standard. Perylene and naphthacene were obtained from Rütgerswerke-Aktiengesellschaft. 9,10-Dimethylanthracene was obtained from L. Light & Co.

Analytical procedure

At constant modulation depth and amplifier gain the signal amplitude (peak to peak height on the recorder trace) is directly proportional to the number of radicals present in the microwave cavity, provided the dielectric absorption of the samples remains the same and saturation effects are absent. For two samples of the same free radical species the signal amplitude is therefore directly proportional to the concentration. This relationship was found to hold for the DPPH radical in benzene solution over a ten-fold range of concentration. The radical concentration in an unknown solution may, therefore, be determined by direct comparison of the recorder trace for the unknown with that for a standard solution of the same radical.

No saturation effects were observed with the polynuclear hydrocarbons under the present experimental conditions when the microwave power was 35 mW. It should be noted that in the determination of relative concentrations by the method described a small degree of saturation can be tolerated, because with two solutions of the same free radical the signal amplitude will be reduced by approximately the same saturation factor.

The following procedure was adopted for the measurements on the polynuclear hydrocarbons. Differing amounts of the hydrocarbon solution were measured with an Agla micrometer syringe into separate sample tubes. Additional solvent was added to bring the level of solution in each tube to about the same height. Activated silica-alumina catalyst, previously placed in approximately the correct amount in small tightly-stoppered tubes, was now added slowly to the hydrocarbon solution using a small funnel, the contents of the tube stirred carefully for several min, and the tube stoppered. If it was found that the depth of active sample was under 19 mm, more catalyst was added and the contents of the tube again stirred carefully. Five or six ESR spectra with a sweep-duration time of 1 min were recorded for each catalyst-hydrocarbon system and the mean value for the signal amplitude was obtained. A series consisting of 30 determinations (*i.e.*, preparation of radical sample and measurement of ESR absorption) showed that the standard deviation of the value obtained for the ESR absorption from a single determination from the arithmetic mean for the series was about 5%. The time required for a complete estimation on a solution of unknown concentration, using two standards, is about 30 min.

The determination of absolute concentrations of radicals requires a comparison to be made with a stable free radical of different structure and the procedure is more complicated than that used for determining relative radical concentrations. The recorded spectrum, which is a first derivative, must be integrated to give the true absorption curve. The relative number of free radicals in the two samples is proportional to the areas under the respective absorption curves. Further integration gives, therefore, the ratio of the number of free radicals in the two systems. The accuracy of this procedure is limited largely by the errors in double integration, provided power-saturation effects are absent. A test of the procedure with perylene solutions is described later.

RESULTS

Anthracene

The spectrum obtained with anthracene adsorbed from carbon disulphide is shown in Fig. 1a. While the spectrum is less well resolved than that obtained with a solution of the hydrocarbon in 98% sulphuric acid, the overall width and observed splittings leave no doubt that the paramagnetic species is the same as that in sulphuric acid and it is identified, therefore, as the radical cation $C_{14}H_{10}^{+}$ formed by electron transfer to a Lewis acid site on the silica-alumina surface.[2] The effect of anthracene concentration on the number of radicals formed is shown in Fig. 2. Over the range 0–20 μg a

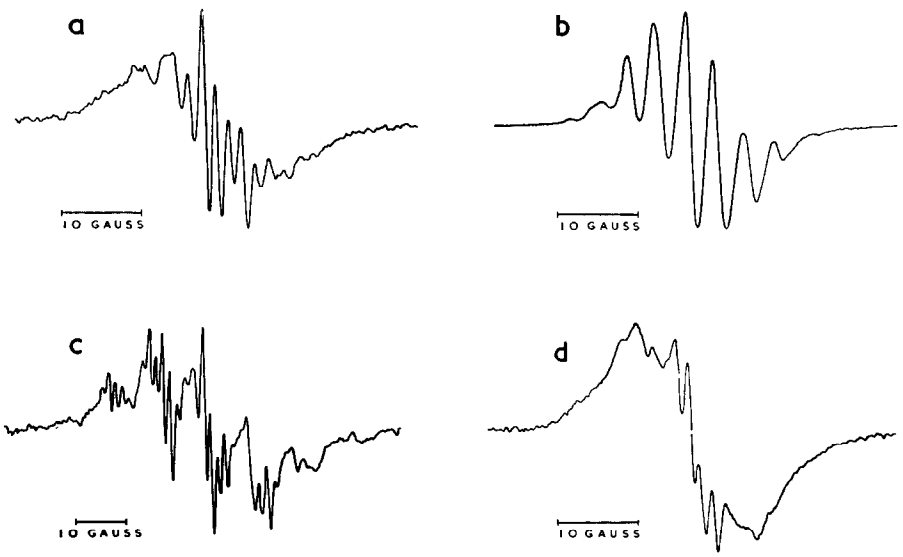


FIG. 1.—Electron spin resonance spectra (first derivative): (a) anthracene, (b) perylene, (c) 9,10-dimethylanthracene (adsorbed from carbon disulphide), and (d) naphthacene (adsorbed from benzene).

closely linear plot is obtained. At higher concentrations conversion into the radical form is incomplete. An unknown solution should therefore be diluted, if necessary after preliminary trial, so that the total hydrocarbon content falls within the stated range. The signal amplitude of the unknown solution may then be compared directly with one or more standard anthracene solutions in the same range.

The stability of the anthracene radical is shown in Fig. 3. In the absence of detectable amounts of unconverted hydrocarbon in solution the radical decays slowly and measurement of the ESR spectrum may be made at any time within 20 min of preparation. In stronger solution decay is rapid. The process involved in the decay is not certain, but may be simple dimerisation involving reaction between a neutral molecule and the radical ion. It is significant that the resolution decreases as the signal decays indicating that new radical species are formed. Decay processes involving two radical-ions seem improbable in view of their charge.

Provided the catalyst-hydrocarbon system is covered with solvent there is no detectable interaction with oxygen and no precautions are necessary to protect the system from the atmosphere or moisture. In the absence of solvent the spectrum undergoes collision broadening with oxygen and no ESR absorption is observable.

This process is strictly reversible, the spectrum being restored when the oxygen is removed.[5] No detectable chemical interaction occurs between oxygen and the adsorbed radical ion in the absence of solvent even after periods up to 24 hr. Either carbon disulphide or benzene may be used as solvent. The colour of the radical in carbon disulphide and in benzene is blue.

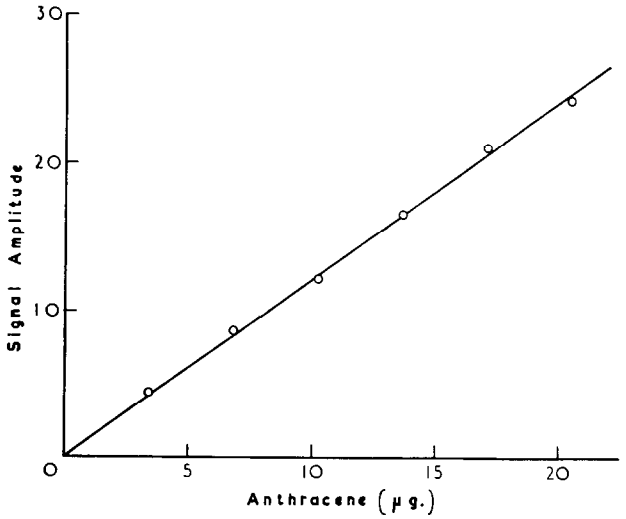


FIG. 2.—Signal amplitude (peak to peak height on the first derivative curve) as a function of concentration for anthracene in carbon disulphide.

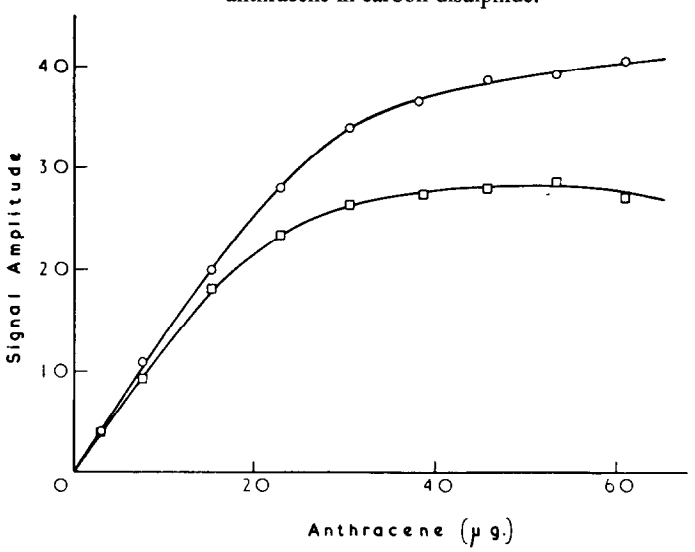


FIG. 3.—Signal amplitude as a function of concentration for anthracene in carbon disulphide. Measurements made within 15 min of radical formation (○) and 1·5 hr later (□).

Perylene

The perylene radical-ion spectrum is shown in Fig. 1b and the adsorption isotherm in Fig. 4. As in the case of anthracene a linear plot is obtained, the useful range being

0–140 μg. The quantitative nature of the conversion with perylene was checked by comparison of the spectrum obtained with a $7 \times 10^{-4}M$ solution of perylene in carbon disulphide with that for a $3 \times 10^{-3}M$ solution of DPPH in dry benzene employing in each case a sweep-duration time of 5 min. The results of a series of determinations, employing conventional techniques for the double integration procedure,

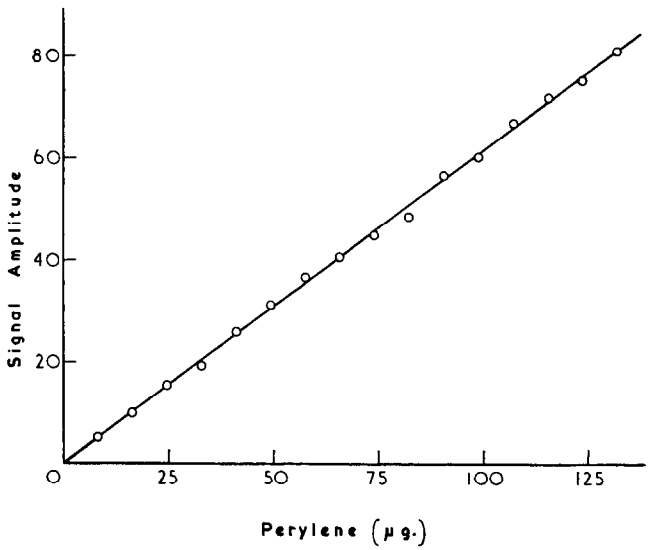


FIG. 4.—Signal amplitude as a function of concentration for perylene in carbon disulphide.

are shown in Table I. Experiments 1–4 indicate that with the well-resolved and reproducible spectra obtained with high signal-to-noise ratio in these experiments, the error involved in this double integration procedure does not exceed $\pm 3\%$. In Experiments 5 and 6 different hydrocarbon and DPPH solutions were employed in the determination. The average error in the complete series of measurements does not exceed $\pm 6\%$. It may be noted that this procedure is not suitable for routine analysis because

TABLE I.—FREE RADICAL CONCENTRATION IN $7{\cdot}0 \times 10^{-4}M$ PERYLENE SOLUTION ON ADDING ACTIVATED SILICA-ALUMINA CATALYST.

Experiment number	Free radical concentration, $M \times 10^4$
1	7·1
2	7·2
3	7·0
4	6·9
5	8·0
6	7·6

the time required for a single determination including the necessary double integration is a matter of hours. Electronic integration would clearly reduce the time involved to manageable levels, although direct comparison with a known hydrocarbon standard is preferable where one is available.

The stability of the perylene radical-ion is greater than that of the corresponding anthracene ion. Over a period of 24 hr the signal amplitude decreases by less than 5%. Unconverted hydrocarbon in solution has no effect on the decay rate of the radical. The perylene radical-catalyst system has a deep violet colour which is detectable even at very low concentration.

9,10-Dimethylanthracene

The spectrum obtained with this hydrocarbon in carbon disulphide is shown in Fig. 1c and the relation between signal amplitude and solution concentration in Fig. 5,

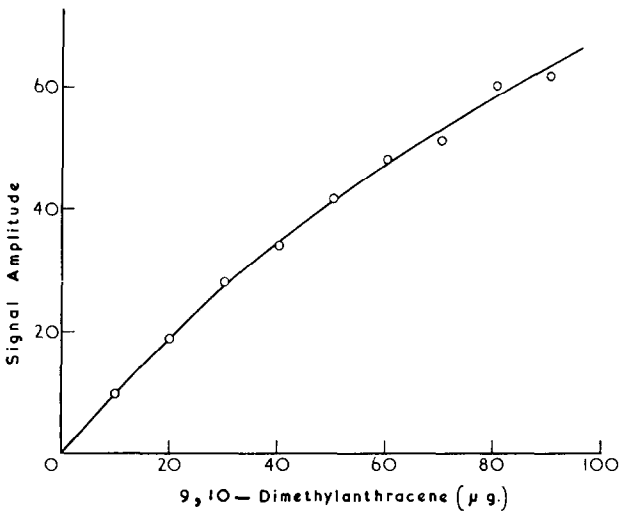


FIG. 5.—Signal amplitude as a function of concentration for 9,10-dimethylanthracene in carbon disulphide.

the useful range extending between 0 and 90 μg. In contrast to the results for anthracene and perylene the plot is slightly curved. To determine accurately the concentration of an unknown solution it would therefore be necessary to compare its signal amplitude with that of a standard dimethylanthracene solution not differing greatly from it in concentration; this may entail the preparation of two standard solutions. Because a solution of 9,10-dimethylanthracene is unstable in daylight, all operations involving the solution including the addition of the catalyst must be performed in a darkroom using a safelight only.

As in the case of anthracene the radical is fairly stable in the absence of detectable amounts of neutral hydrocarbon in solution and measurement of the ESR spectrum may be made at any time within 20 min of preparation. In strong solutions where unadsorbed hydrocarbon is present, the ESR signal decays rapidly in intensity and in resolution indicating that new radical species are formed. The dimethylanthracene radical-ion in carbon disulphide and in benzene is green.

Naphthacene

The ESR spectrum is shown in Fig. 1d and the signal amplitude-concentration plot in Fig. 6. The useful range extends between 0 and 200 μg; over this range the plot

is slightly curved. Naphthacene in solution in carbon disulphide or benzene undergoes rapid photochemical oxidation in daylight and it was thought that the radical-ion in this case might be too unstable for analytical purposes. In fact the adsorbed radical has a remarkably high degree of stability, decaying less than 2% in 24 hr. Until the radicals are formed all operations must be carried out in the darkroom using a safe-light. The naphthacene radical-catalyst system has a bright green colour in benzene and in carbon disulphide.

DISCUSSION

The strong absorption in the ultraviolet and the intense fluorescence of many polynuclear hydrocarbons provide widely used analytical methods for their detection and

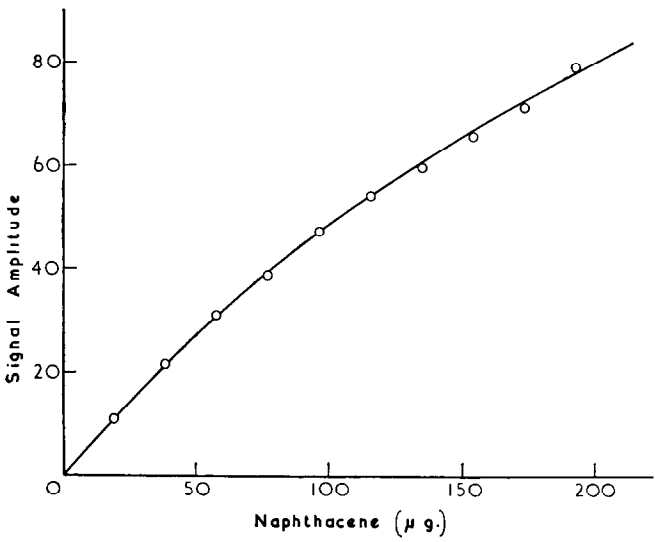


FIG. 6.—Signal amplitude as a function of concentration for naphthacene in benzene.

estimation.[6] The electron spin resonance technique now described provides an alternative analytical method of high sensitivity and with an accuracy which compares favourably with other spectroscopic techniques at low concentrations. The method depends for its success on the quantitative nature of radical formation on a silica-alumina surface and on the stability of the resulting radical-ion species. The stabilising effect on free radical species of surface adsorption has been noted previously by Bijl, Kainer and Rose-Innes,[7] who reported marked stabilisation of semiquinone radicals adsorbed on alumina or silica gel. The observation that conversion into the radical form is complete within the limit of experimental error over a wide range of concentration for each of the hydrocarbons studied is of interest in view of the suggestion by Aalbersberg, Hoijtink, Mackor and Weijland[8] that two different species are formed by the reaction of aromatic hydrocarbons with strong Lewis acids, *viz.*, covalent complexes, in which there are no uncoupled electron-spins, and radical cations. Clearly the evidence does not support this contention for silica-alumina.

The useful concentration ranges for a particular catalyst sample in the technique now described depends entirely on its activity as an electron-acceptor. The catalyst used in these experiments was a commercial cracking catalyst readily obtainable in this

country. More active catalysts have been described[9] for which the useful range would be greatly extended.

Because the g-factors of the hydrocarbon radicals all lie close to the free-spin value of 2·0023, considerable overlap of the spectra occurs with consequent mutual interference. Similar difficulties occur with fluorescence methods.[10] On the other hand, because benzene is inert to silica-alumina and because conversion into the radical form with naphthalene is negligible under the conditions of these experiments,[5] neither of these hydrocarbons interfere with the determination. In the case of naphthacene the electron spin resonance method has some advantage over conventional techniques. Solutions of this hydrocarbon in inert solvents undergo rapid photochemical oxidation in the light. When converted into the free radical form on the other hand naphthacene is surprisingly stable, only a marginal decrease in signal intensity being observed in 24 hr. This stabilisation in the free radical form is the more remarkable because the photochemical oxidation in solution may be assumed to involve excited species.

The application of this technique to the estimation of polynuclear hydrocarbons is limited to those which are converted readily into the free radical form. The ease with which this occurs on a silica-alumina surface varies widely and is a direct measure of the electron affinity of the hydrocarbon. This aspect is being further investigated and will be described elsewhere.

Acknowledgement—The authors thank Mr. R. K. Quigg for skilled assistance with the electronic instrumentation.

Zusammenfassung—Gewisse, vielkernige Kohlenwasserstoffe werden an der Oberfläche stark dehydrierter Silikat-Aluminiumoxyd-Katalysatoren quantitativ in freie Radikale verwandelt. Die Radikale sind beständig, solange sie an der Oberfläche des Katalysators adsorbiert sind und können mittels Elektronenspinresonanz bestimmt werden. Weniger als 10^{-10} Mole Kohlenwasserstoff kann bestimmt werden. Anwendung der Methode auf die Bestimmung von Anthrazen, Perylen, Dimethylanthrazen und Naphthazen wird beschrieben.

Résumé—Certains hydrocarbures polynucléaires sont transformés quantitativement en radicaux libres lorsqu'ils sont adsorbés à la surface d'un catalyseur constitué d'un mélange fortement deshydraté de silice et d'alumine. Les radicaux libres formés sont stables à l'état adsorbé et leur détection et leur dosage par résonance paramagnétique électronique sont décrits. Moins de 10^{-10} moles d'hydrocarbure peuvent être décelées. Le dosage quantitatif de l'anthracène, du pérylène, du diméthylanthracène et du naphtacène par cette technique est décrit.

REFERENCES

[1] J. A. Pople, W. G. Schneider and H. J. Bernstein, *High-resolution Nuclear Magnetic Resonance*. McGraw-Hill, New York, 1959.
[2] J. J. Rooney and R. C. Pink, *Proc. Chem. Soc.*, 1961, 70.
[3] D. M. Brouwer, *Chem. and Ind.*, 1961, 177.
[4] For a description of a similar spectrometer see D. J. E. Ingram, *Free Radicals as Studied by Electron Spin Resonance*. Butterworths, London, 1958, p. 81.
[5] J. J. Rooney and R. C. Pink, *Trans. Faraday Soc.*, 1962, **58**, 1632.
[6] A. Weissberger, *Technique of Organic Chemistry, Vol. 9: Chemical Applications of Spectroscopy*. Interscience, New York, 1956.
[7] D. Bijl, H. Kainer and A. C. Rose-Innes, *Nature*, 1954, **174**, 830.
[8] W. I. J. Aalbersberg, G. J. Hoijtink, E. L. Mackor and W. P. Weijland, *J. Chem. Soc.*, 1959, 3055.
[9] R. M. Roberts, C. Barter and H. Stone, *J. Phys. Chem.*, 1959, **63**, 2077.
[10] See, for example, G. A. Thommes and E. Leininger, *Talanta*, 1961, **7**, 181.

Talanta, 1962, Vol. 9, pp. 939 to 945. Pergamon Press Ltd. Printed in Northern Ireland

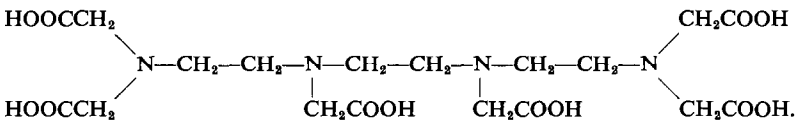
PRELIMINARY COMMUNICATIONS

Triethylenetetramine-N,N,N′,N″,N‴,N‴-hexa-acetic acid as a new titrimetric reagent

(*Received* 2 *July* 1962. *Accepted* 20 *August* 1962)

FROM the great number of polyaminocarboxylic acids which have been synthesised during the last two decades, the disodium acid of ethylenediaminetetra-acetic acid (EDTA) has been the most used as a titrimetric reagent. To a considerably smaller extent, and usually only in special cases, a few other acids have also been used, *e.g.*, 1,2-diaminocyclohexane-N,N,N′,N′-tetra-acetic acid (DCyTA), 1,2-diaminopropane-N,N,N′,N′-tetra-acetic acid (Methyl-EDTA, MEDTA), diethylenetriamine-N,N,N′,N″,N″-penta-acetic acid (DTPA), ethylene glycol-bis(β-aminoethyl ether)-N,N′-tetra-acetic acid (EGTA).

A most interesting substance has proved to be triethylenetetramine-N,N,N′,N″,N‴,N‴-hexa-acetic acid (TTHA), synthesised recently in the laboratories of Geigy Chemical Company (Basel, Switzerland)



This hexabasic acid offers for co-ordination bonding with metals four lone pairs of nitrogen electrons. Hence all requirements even for the formation of bimetallic complexes of the type Me_2X are fulfilled. Because of the supposed structure (formation of five and six-membering rings) it was possible to assume that the stability of the complexes formed would be very high and similar to the complexes with EDTA. This was confirmed by preliminary titrations with a solution of the disodium salt of TTHA at the same pH as in EDTA titrations, using the same very sensitive metallochromic indicators, *e.g.*, Xylenol Orange, Methylthymol Blue, Thymolftalexon, Fluorexon (Calcein), Eriochrome black T and Murexide.

EXPERIMENTAL

Reagents

0·05*M solution of the disodium salt of TTHA*: Prepared by dissolving 24·723 g of the acid (Geigy Chemical Company, Basel, Switzerland) in 130 ml of 1*M* sodium hydroxide solution in the warm, and diluting to 1 litre with redistilled water.

0·05*M solutions of metallic salts:* Prepared by dissolving the appropriate amounts of reagent grade chemicals (chloride, nitrate or sulphate) in redistilled water. The strengths of the solutions were checked complexometrically.

Indicators: 0·5% aqueous solutions of Xylenol Orange, Fluorexon(Calcein), Thymolftalexon and Eriochrome Black T as mixtures with potassium nitrate (1:100).

Other reagents included 1*M* nitric acid, 1*M* potassium hydroxide, concentrated aqueous ammonia, ammonia buffer, solid urotropine.

Titration of metals

The determination of single metals was carried out at similar pH values to those for EDTA titrations. In many cases two or even three methods of determination were chosen to ascertain the eventual influence on the formation of bimetallic complexes. The results are summarised in Table I.

TABLE I.—TITRATION OF VARIOUS METALS WITH TTHA

Metal	pH of the solution	Indicator	Back titration with	Composition of complex	Remarks
Bi	1–2	XO	Direct	1:1	
	3–4	XO	Th	1:1	
Th	3–4	XO	Direct	1:1	
Tl^{III}	3–3·5	XO	Direct	1:1	At 50–60°
	3–3·5	XO	Th	1:1	
	5–5·5	XO	Pb	1:1	
Zr	3–4	XO	Th	1:1	Slight displacement at the end-point, then indicator blocking
Ti	5–5·5	XO	Pb	2:1	As peroxocomplex
Ga	3–4	XO	Th	2:1	
	5–5·5	XO	Pb	2:1	
In	3–5	XO	Direct	1:1	In the hot
	5–5·5	XO	Pb	1:1	
	9·5	ERIO T	Direct	1:1	Sluggish end-point in the presence of tartaric acid
Sn^{II}	3–4	XO	Th	2:1	
Sn^{IV}	3–4	XO	Th	1:1	Slight displacement
Al	5–5·5	XO	Pb	2:1	After boiling with TTHA
Cr	5–5·5	XO	Pb	2:1	After boiling with
	10–11	FRX	Ca	—	TTHA. Displaced
La	5·5	XO	Direct	1:1	
Pb	5·5	XO	Direct	2:1	
Zn	5·5	XO	Direct	2:1	
	9–10	ERIO T	Direct	2:1	
Cd,Cu,Co,Ni	5·5	XO	Pb	2:1	
Co, Ni	10–12	THFX FRX	Ca	2:1	
Ni	10–11	MUR	Direct	2:1	
Hg	5·5	XO	Direct	2:1	
Mn	10–11	THFX	Direct	1:1	
	10–12	FRX	Ca	1:1	
Ca	10–12	THFX	Direct	1:1	
	10–12	FRX	Direct	1:1	
Mg	9	THFX	Direct	2:1	In TEA solution free of salts and in the presence of alcohol

XO = Xylenol Orange, THFX = Thymolftalexon, FRX = Fluorexon, ERIO T = Eriochrome Black T, MUR = Murexide, TEA = Triethanolamine.

DISCUSSION

Triethylenetetramine-N,N,N′,N″,N‴,N‴-hexa-acetic acid forms with the majority of bivalent elements bimetallic complexes of the type Me_2X^{2-}, with the exceptions of manganese and calcium which form 1:1 complexes in an alkaline medium. It seems that magnesium under limited conditions can form a 2:1 complex. Tervalent metals also form bimetallic complexes (probably Me_2X^0), excepting tervalent thallium, indium, bismuth and lanthanum, which form 1:1 complexes. Their existence, over a wide range of pH, has been proved by titrations in acidic and alkaline media. As expected, tervalent elements form 1:1 complexes. The only exception is titanium, which in the presence of hydrogen peroxide forms a 2:1 complex with TTHA. The existence of a similar zirconyl-peroxocomplex has not been proved with certainty. Among the more common elements, bi- and tervalent iron behave quite exceptionally. By back-titration with bismuth, thorium or lead, displacement of iron from the complex always took place and the function of the indicator failed.

Similarly, the TTHA complex of tervalent cobalt is formed slowly and non-quantitatively. Scandium likewise forms a 1:1 complex and is co-titrated with thorium. It is displaced quantitatively from its complex at pH 1–2 by bismuth. In slightly acidic solutions (pH 5) scandium reacts with Xylenol Orange even in the presence of excess TTHA.

From our experiments it appears that TTHA is at present the only compound of the complexan type forming sufficiently stable bimetallic complexes which can be used for titrimetric analysis. The different behaviour of bivalent and tervalent metals with TTHA can be applied for practical purposes. As an example the determination of a mixture of bismuth and lead is given.

Both of these elements form with EDTA only 1:1 complexes. Lead forms with TTHA a 2:1 complex, however, like other bivalent elements (see Table I). It is therefore possible to determine by two titrations, with EDTA and TTHA, the sum of both with great accuracy—theoretically regardless of their concentration ratios. Both titrations are carried out under the same acidity conditions with the same indicator. Results of these determinations together with the *Procedure* are given in Table II.

TABLE II.—DETERMINATION OF A MIXTURE OF BISMUTH AND LEAD WITH EDTA AND TTHA

Taken, *ml*		EDTA added,	Back titration with $Pb(NO_3)_2$,	TTHA added,	Back-titration with $Pb(NO_3)_2$,	Found, *ml*	
Bi	Pb	*ml*	*ml*	*ml*	*ml*	Bi	Pb
0·98	0·98	2·97	0·98	2·97	2·94	0·99	0·98
4·89	4·90	11·88	1·99	11·88	9·01	4·87	5·02
0·98	4·90	6·93	1·06	5·94	5·08	1·03	4·84
4·89	0·98	6·93	1·03	6·93	2·95	5·02	0·88
9·78	0·98	14·85	4·07	14·85	9·03	9·90	0·88
0·98	9·80	14·85	4·07	6·93	2·05	1·04	9·74
0·98	9·80	14·85	4·07	14·85	18·00	0·92	9·86
4·89	19·60	26·73	2·23	16·83	4·31	4·86	19·64
14·67	1·96	19·80	3·25	20·79	10·20	14·83	1·72

To the acid solution (0·05*M*) of bismuth and lead add an excess of 0·05*M* EDTA, adjust the pH to 5–5·5 with solid urotropine and titrate with 0·05*M* lead nitrate solution using Xylenol Orange as indicator. Carry out a second titration on a further aliquot of the mixture under the same conditions using 0·05*M* TTHA.

Table I shows further possibilities of such new determinations of mixtures of two elements which do not require screening reagents, *e.g.*, thorium-titanium, gallium-indium, tin^{II}–tin^{IV}, and generally, the combination of Me_1^{II}–Me_1^{III}, and finally, the determination of a tervalent element in the presence of a bivalent element and *vice versa*. From the analytical point of view special attention should be paid to the different behaviour of bivalent manganese (1:1 complex), magnesium (2:1) and calcium (1:1).

Theoretically very interesting are equilibria of the types:

$$Me_2X + 2Y \rightleftarrows 2MeY + X \quad (1)$$

$$MeX + Y \rightleftarrows MeY + X \quad (2)$$

where X and Y are the anions of the acids TTHA and EDTA (charges are omitted), respectively. The equilibrium is reached very quickly in the case of substitution labile complexes. The reaction shifts quantitatively to the right provided that the difference in stability of the complexes Me_2X and MeY is sufficient. In a substitution stable complex the reaction of Me_2X or MeX with Y proceeds,

however, with an analytically immeasurable velocity. In such cases the cation Me is actually blocked or masked by the anion X. This phenomenon has also been observed with the complexes BiX, Al_2X and Ni_2X, while reaction (1) proceeds practically quantitatively for similar complexes with lead or tervalent iron.

It is possible to follow reaction (1) by titration with the solution of a salt of a metal which forms with both X and Y only 1:1 complexes. If reaction (1) proceeds quantitatively, 2Y are substituted for 1X and the titration consumption drops by one half. For orientation experiments 0·05*M* lanthanum nitrate solution has been used as a titrant with Xylenol Orange at pH 5–5·7 (urotropine). In this way it is possible to determine, for example, such binary mixtures as iron–aluminium, iron–nickel, nickel–lead, nickel–cadmium, nickel–zinc, *etc.*, because only the complexes Fe_2X, Pb_2X, Cd_2X, Zn_2X, *etc.*, react quantitatively according to equation (1).

Determination of iron and nickel

Procedure: In one aliquot determine the sum of the metals by back-titration of excess EDTA with lead nitrate solution using Xylenol Orange as indicator. To a second aliquot add a measured volume of TTHA and then EDTA. The excess of both is now titrated with lanthanum nitrate solution (Xylenol Orange). The TTHA is bound only to one metal (*e.g.* nickel), then EDTA to the other one (*e.g.* iron).

Calculation:

(a) 1 mole of iron or 1 mmole of nickel corresponds to 1 mmole of EDTA.
(b) 1 mole of nickel corresponds to 0·5 mmole of TTHA.
(c) 1 mmole of EDTA or TTHA corresponds to 1 mmole of lanthanum.

The second reaction can be followed by titration with a metal which forms with TTHA a 2:1 complex. If the reaction proceeds quantitatively, then consumption of titrant doubles, because Y replaces X which forms only Me_2X-complexes. For these titrations 0·05*M* lead nitrate solution and Xylenol Orange were used (pH 5·5-urotropine). In this way a mixture of iron and bismuth can be analysed because the BiX does not react with EDTA.

Determination of iron and bismuth

Procedure: In one aliquot determine the sum of iron plus bismuth complexometrically, *e.g.*, by back-titration of excess EDTA with bismuth nitrate solution at pH 1–2 with a Xylenol Orange end-point. To a second aliquot add a measured volume of TTHA and then EDTA. After adjusting the pH with urotropine, determine the excess of TTHA and EDTA with lead nitrate solution.

Calculation:

(a) 1 mmole of iron or bismuth corresponds to 1 mmole of EDTA.
(b) 1 mmole of bismuth corresponds to 1 mmole of TTHA.
(c) 1 mmole of lead corresponds to 0·5 mmole of TTHA (or 1 mmole of EDTA).

Determination of aluminium and iron

Procedure: To 5 ml of a 0·05*M* solution of aluminium and iron 10 ml of 0·05*M* TTHA were added and after boiling for 1–2 min and cooling, 12 ml of 0·05*M* EDTA were added. The solution was titrated with 14·5 ml of lanthanum nitrate solution to a Xylenol Orange end-point. As the sum of TTHA and EDTA (10 plus 12) corresponds to 22 ml of lanthanum solution, the sum is now Al_2X and FeY = 22 − 14·5 = 7·5 ml. The sum of AlY and FeY (titration with EDTA) corresponds to 10 ml. The difference of both titrations 10 − 7·5 multiplied by 2 (5 ml) gives the amount of aluminium. The difference 10 − 5 ml gives the amount of iron.

A number of other determinations of mixtures of two to three elements have been carried out, based on the above mentioned principles which do not require the use of masking reagents. Our further experiments with the combination of different new masking reagents are showing other unexpected possibilities of a highly selective determination of elements as well as the analysis of very complicated mixtures. Results of this further research will be published in due course.

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Summary—The disodium salt of triethylenetetramine-N,N,N′,N″,N‴,N‴-hexa-acetic acid (TTHA) has been used for complexometric determination of a great number of metals and the existence of bimetallic complexes of most bivalent elements has been proved. Tervalent elements form bimetallic complexes too, except for bismuth, thallium, indium and lanthanum. By using EDTA and TTHA it is possible to determine some binary mixtures of elements without screening reagents. The new types of displacement reactions:

$$Me_2X + 2Y \rightleftarrows 2MeY + X$$

$$MeX + Y \rightleftarrows MeY + X$$

(X and Y are the anions of TTHA and EDTA) can be used for complexometric analysis. These possibilities are briefly discussed.

Zusammenfassung—Das Dinatriumsalz der Triäthylentetramin-hexaessigsäure (TTHE) wurde zur komplexiметrischen Bestimmung einer grossen Zahl von Metallen herangezogen. Tervalente Metalle formen bimetallische Komplexe, mit der Ausnahme von Bi, Th, In und La. Durch die Verwendung von TTHE in Verbindung mit ÄDTE ist es möglich Metallpaare ohne Maskierungmittel zu erfassen. Der neue Typ von Verdrängungsreaktionen:

$$Me_2X + 2Y \rightleftharpoons 2MeY + X$$

$$MeX + Y \rightleftharpoons MeY + X$$

(X und Y stehen für die Anionen von TTHE und ÄDTE) kann zur komplexiметrischen Bestimmung herangezogen werden. Diese Möglichkeiten werden kurz diskutiert.

Résumé—Le sel disodique de l'acide triéthylène tétramine héxacétique (TTHA) a été utilisé pour le dosage complexométrique d'un grand nombre de métaux. L'existence de complexes bimétalliques avec la plupart des éléments bivalents a été demontrée. Ces éléments trivalents forment également des complexes bimétalliques à l'exception du bismuth, du thallium, de l'indium et du lanthane. Grâce à l'emploi de l'E.D.T.A. et du T.T.H.A il est possible de doser des mélanges d'éléments sans avoir à utiliser des agents complexants. Les réactions du type:

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(X et Y désignant les anions du T.T.H.A. et de l' E.D.T.A), peuvent être utilisés pour des dosages complexométriques. Les possibilités de la méthode sont brièvement discutées.

4-(2-Pyridylazo)resorcinol as a selective and sensitive spectrophotometric reagent for niobium[V]

(*Received* 17 *July* 1962. *Accepted* 19 *July* 1962)

WEHBER[1], and Sommer and Hniličková[2] examined 4-(2-pyridylazo)resorcinol (PAR) as a potential metallochromic reagent for several ions. The PAR molecule, in neutral or acid solution, exhibits a yellow colour, and reacts to form red chelates with a great number of ions including Pb, Zn, Cd, Cu, Ni, Co, Hg^{II}, U^{VI}, Pd^{II}, Y, La, In, Nd, Er, Zr and Ti. The colour reactions of many PAR complexes have been studied very fully by Pollard and his coworkers[3]. With the exception of those with uranium^{VI} and nickel, all these compounds are very readily broken down by ethylene diaminetetra-acetic

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acid (EDTA), and consequently PAR is an excellent metallochromic indicator for most of these ions.[4,5,6]

We have studied some of the reactions of this reagent with other metal ions, and find that it may be used as a very selective reagent for the spectrophotometric determination of trace amounts of niobium^{V} in a tartrate-buffered medium at pH 5·8. We have established by a variety of procedures that PAR reacts with niobium^{V} to form a moderately stable 1:1 red complex which absorbs strongly over a fairly broad and smooth absorption band (λ_{max} 5500 Å), and which, by our procedure, obeys the Lambert-Beer relationship over the range 0–70 μg Nb in a final volume of 100 ml. The effect of twenty-fold amounts of over thirty common cations and seven anions has been studied, and we have found that EDTA acts as a general masking agent. Tantalum forms only a very weakly coloured complex, and in the presence of sufficient tartrate up to a twenty-fold excess of this element (50 μg of Nb^{V}: 1000 μg of Ta^{V}) may be tolerated. Uranium and vanadium interfere by forming red complexes. Cyanide may be added to mask silver (which only forms a weak EDTA complex), and to break down the pink EDTA complex of cobalt^{II}. Cerium^{IV}, if present, should be reduced to cerium^{III} with ascorbic acid. None of the common anions interferes, and only phosphate, sulphide and sulphite cause difficulty. The order of addition of the various reagent solutions is important when certain foreign cations are present.

The colour reaction has been studied and the conditional stability constant of the PAR-Nb^{V} complex has been evaluated by two independent methods: the molecular extinction coefficient and the sensitivity index have also been measured. The colour system develops rapidly at room temperature, and is stable indefinitely once formed; the optimum pH range is not very critical. We have compared this new method for the spectrophotometric determination of niobium^{V} with the standard thiocyanate and 8-hydroxyquinoline procedures and find it to compare favourably in terms of ease of application, sensitivity, freedom from interference, range of application and stability. The method is now undergoing further examination in our laboratory, and independent examination by other workers. These, and other aspects of the procedure will be reported fully in the near future.

Meanwhile it may be noted that the reagent provides an elegant and sensitive spot test for niobium. The detection limit in a small test-tube or spot-plate is 0·1 μg, and the dilution limit is 1 part in 2,500,000. The colour reaction should be allowed to proceed for 1–2 min at room temperature, or the solution should be warmed (test-tube), whereupon the colour reaction is instantaneous.

The following ions do not interfere even when present in *ca.* twenty-fold excess: Pb, Bi, Cd, Hg^{II}, Fe^{III}, Fe^{II}, Al, Cr^{III}, Zn, Mn, Ca, Sr, Ba, Mg, Be, Sn^{II}, Sn^{IV}, As, Zr, Cu^{II}, Th, Ta, Ti, La, Ce^{III}, Mo, W, provided that sufficient amounts of EDTA and tartrate are present to maintain them in solution as their colourless or near-colourless complexes. If silver or cobalt is present, cyanide should be added to mask them. The EDTA must be added before the PAR and buffer, particularly when nickel is present, because this ion forms a complex with PAR which is not broken down by EDTA when this is added subsequently. Zirconium should be protected by EDTA before the buffer is added. It is the acetate ion of the buffer which is the effective masking agent for thorium.

SPOT TEST PROCEDURE

Reagents

10^{-3}M *PAR solution:* 0·2951 g of PAR, disodium salt, per litre of solution.

2×10^{-2}M *EDTA:* 7·445 g of disodium EDTA dihydrate in 1 litre of solution.

Buffer, pH 5·8: 150 g of sodium acetate trihydrate + 4·6 ml of glacial acetic acid in 1 litre of solution.

Procedure

To a drop of test solution containing $>0{\cdot}1$ μg of niobium in a sodium tartrate medium (*ca.* pH 5·8–6·4) in a small test-tube (or spot-plate) add 1 drop of EDTA followed by 1 drop of PAR and two drops of buffer. Warm gently on a hot water bath, or (spot-plate) allow to stand for 1–2 min. Carry out a blank test at the same time. The blank remains yellow, but the niobium-containing solution develops an orange to red colour depending on the amount of niobium present. The order of addition of reagents is important.

Acknowledgement—We wish to thank Dr. F. H. Pollard of the University of Bristol for providing us with a very pure sample of PAR.

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Summary—The reagent 4-(2-pyridylazo) resorcinol, PAR, in the presence of EDTA, gives a colour reaction with quinquevalent niobium which is not interfered with by any of the metals which normally accompany niobium. Of some 30 cations examined, only uranium^{VI} and vanadium^{V} interfere seriously. The reaction provides a sensitive method for the spectrophotometric determination of niobium, and is also applicable as a spot-test for amounts of niobium^{V} down to 0.1 μg. Even tantalum does not interfere when present in twenty-fold amounts, provided sufficient tartrate ion is added.

Zusammenfassung—4-(2-Pyridylazo)resorcinol (PAR) gibt in Gegenwart von ÄDTE mit fünfwertigem Niob eine Farbreaktion, die durch keines der mit Niob üblicherweise vorkommenden Metalle gestört wird. Von etw 30 untersuchten Kationen geben nur Uran(VI) und Vanadin(V) starke Störungen. Die Reaktion kann zu einer empfindlichen, spektrophotometrischen Bestimmung von Niob herangezogen werden und ist auch als Tüpfeltest bis herab zu 0.1 μg Nb verwendbar. Auch Tantal stört nicht, vorausgesetzt seine Menge überschreitet nicht das Zwanzigfache des Niob und genügend Weinsäure ist anwesend.

Résumé—Le 4 (2-pyridylazo) résorcinol, PAR, donne en présence d'E.D.T.A un composé coloré avec le niobium (V). Aucun des métaux qui accompagnent habituellement le niobium ne gêne. Parmi quelques 30 cations étudiés, seul l'uranium (VI) et le vanadium (V) gênent d'une façon notable. Cette réaction permet la mise au point d'une méthode sensible de dosage du niobium par spectrophotométrie; elle permet aussi de déceler le niobium (V) jusqu'à 0,1 μg. En présence de tartrate le tantale ne gêne pas même présent en quantités vingt fois supérieures.

REFERENCES

[1] P. Wehber, *Z. analyt. Chem.*, 1957, **158,** 10.
[2] L. Sommer and M. Hniličková, *Naturwiss.*, 1958, **45,** 544.
[3] F. H. Pollard, P. Hanson and W. J. Geary, *Analyt. Chim. Acta*, 1959; **20,** 26, W. J. Geary, G. Nickless and F. H. Pollard, *ibid.*, 1962, **26,** 575.
[4] F. J. Langmyhr and H. Kristiansen, *ibid.*, 1959, **20,** 524.
[5] P. Wehber, *Z. analyt. Chem.*, 1959, **166,** 186.
[6] *Idem, ibid.*, 1958, **163,** 104.

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SHORT COMMUNICATIONS

Pyrohydrolytic determination of fluoride in milligram quantities of plutonium fluorides

(*Received* 22 *March* 1962. *Accepted* 25 *June* 1962)

AMONG the methods available for the determination of the fluoride content of heavy metal fluorides two have found common use, *viz.* pyrohydrolysis[1,2,3,4,5,6] in a platinum, nickel or quartz apparatus, and distillation from sulphuric acid in a glass apparatus.[7,8] These methods, although straightforward when used on non-radioactive materials, present some experimental difficulties during the analysis of plutonium fluorides inside completely enclosed glove boxes. A modification of the pyrohydrolytic method was published by Powel and Menis[9] in which the heavy element fluoride is hydrolysed by heating in a current of moist oxygen. Because the use of a moist gas instead of steam has several advantages for work in glove boxes, *e.g.*, it avoids the condensation of steam on the panels and the use of a preheater assembly, the method has been tested on plutonium fluoride.

A sample of plutonium tetrafluoride was heated in a silica reactor tube at 800° in a current of moist air. The liberated hydrogen fluoride was absorbed in dilute sodium hydroxide solution, then determined using the zirconium-alizarin lake spectrophotometrically at 525 mμ.[10]

The precision of the method was determined by 12 analyses of a sample of plutonium tetrafluoride (obtained by the dry hydrofluorination of plutonium dioxide) which had been stored for several months. The mean fluoride content was found to be 22·8% (with a standard deviation of ±1%) compared with the theoretical value of 24·1%.

Because the mean fluoride content obtained from the precision analyses showed a significant bias from the theoretical, it was assumed that the fluoride content had decreased on long storage of the sample. Therefore, for ascertaining the accuracy of the method, a fresh sample of pure plutonium tetrafluoride was prepared and analysed six times. The results (Table I) indicate that the method gives a precision and accuracy of about 1%.

TABLE 1

Wt. of sample, *mg*	Wt. of oxide left behind, *mg*	Fluoride obtained, *μg*	Theoretical fluoride from wt. of oxide, *μg*	Fluoride in the sample, %
1·58	1·38	388	387	24·6
1·26	1·07	291	300	23·1
2·50	2·14	590	600	23·6
2·07	1·76	490	494	23·7
3·24	2·79	770	782	23·8
2·21	1·89	532	530	24·1
Mean	—	—	—	23·8
Theoretical	—	—	—	24·1

Acknowledgement—The authors wish to express their grateful thanks to Dr. G. A. Welch for his interest in this work.

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Summary—The pyrohydrolytic determination of fluoride using moist air is described for the fluoride content of plutonium fluorides on the milligram scale.

Zusammenfassung—Die pyrohydrolytische Bestimmung in feuchter Luft wird für den Fluoridgehalt von Milligrammengen Plutoniumfluorides beschrieben.

Résumé—Les auteurs décrivent le dosage par pyrohydrolyse du fluor contenu dans les fluorures de plutonium à l'échelle due milligramme.

REFERENCES

[1] J. C. Warf *et al.*, *Analyt. Chem.*, 1954, **26**, 342.
[2] J. E. Lee *et al.*, *ibid.*, 1956, **28**, 1441.
[3] C. D. Susano *et al.*, *ibid.*, 1955, **27**, 453.
[4] G. M. Gills, *et al.*, AERE C/M 225, Oct., 1954.
[5] N. Parker and G. A. Welch, WSL-R-36 (declassified reprint).
[6] J. G. Surak *et al.*, *Analyt. Chem.*, 1960, **32**, 117.
[7] H. H. Willard and O. B. Winter, *Ind. Eng. Chem., Analyt.*, 1933, **5**, 7.
[8] B. B. Murray, DP–247, Nov., 1957.
[9] R. H. Powel and O. Menis, *Analyt. Chem.*, 1958, **30**, 1546.
[10] H. E. Bumsted and J. C. Wells, *ibid.*, 1952, **24**, 1595.

Separation and determination of microgram or submicrogram quantities of gold in copper: Use of mercury as a collector

(*Received* 27 *April* 1962. *Accepted* 16 *July* 1962)

INTRODUCTION

SEVERAL methods[1] have been reported for separating trace amounts of gold from aqueous solution. These include coprecipitation with tellurium, lead sulphide or a mixture of mercury and mercury amino salt,[2] extraction with ethyl ether, ethyl acetate[3] or dithizone,[4] *etc.* In the present paper, a new method of separation is proposed and applied to the determination of trace amounts of gold in copper metal. After dissolution of copper metal in nitric and hydrochloric acids, the solution is made ammoniacal. A small amount of mercury is added and the solution is stirred with a magnetic stirrer. Gold is collected into mercury globules as a dilute amalgam, leaving copper in the solution. The amalgam thus obtained is then separated, heated at 350° in a stream of nitrogen to remove mercury, and gold in the residue is determined by the photometric *p*-dimethylaminobenzylidenerhodanine method.[3,5]

EXPERIMENTAL

Apparatus

Hirama model II photoelectric filter photometer with 1-cm cells (0·5–6 μg of gold).
Hirama micro photoelectric filter photometer with 2-cm cells (0·1–0·5 μg of gold).
Atomic and Riken well-type scintillation counters.

Reagents

Mercury: Purify by aeration, washing with dilute nitric acid, and finally vacuum distillation.
Standard gold solutions (5 μg *and* 0·4 μg *of gold per ml*): Dissolve pure gold foil in *aqua regia*, and dilute with 1*M* hydrochloric acid.
Gold-198 *solution:* Dissolve gold-198 in *aqua regia*, and dilute with 1*M* hydrochloric acid or standard gold solutions. Determine the gold concentration photometrically.
Standard silver solution (50 μg *of silver per ml*): Dissolve silver nitrate in 0·1*M* nitric acid.
4% (w/v) *Sodium chloride solution.*
1% *and* 0·5% (w/v) *Sodium fluoride solutions.*
Rhodanine solution: 0·003% *p*-dimethylaminobenzylidenerhodanine in absolute ethyl alcohol.
All of the reagents used were of reagent grade. Water purified by ion-exchange was used throughout the work.

Summary—The pyrohydrolytic determination of fluoride using moist air is described for the fluoride content of plutonium fluorides on the milligram scale.

Zusammenfassung—Die pyrohydrolytische Bestimmung in feuchter Luft wird für den Fluoridgehalt von Milligrammengen Plutoniumfluorides beschrieben.

Résumé—Les auteurs décrivent le dosage par pyrohydrolyse du fluor contenu dans les fluorures de plutonium à l'échelle due milligramme.

REFERENCES

[1] J. C. Warf *et al.*, *Analyt. Chem.*, 1954, **26**, 342.
[2] J. E. Lee *et al.*, *ibid.*, 1956, **28**, 1441.
[3] C. D. Susano *et al.*, *ibid.*, 1955, **27**, 453.
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INTRODUCTION

SEVERAL methods[1] have been reported for separating trace amounts of gold from aqueous solution. These include coprecipitation with tellurium, lead sulphide or a mixture of mercury and mercury amino salt,[2] extraction with ethyl ether, ethyl acetate[3] or dithizone,[4] *etc.* In the present paper, a new method of separation is proposed and applied to the determination of trace amounts of gold in copper metal. After dissolution of copper metal in nitric and hydrochloric acids, the solution is made ammoniacal. A small amount of mercury is added and the solution is stirred with a magnetic stirrer. Gold is collected into mercury globules as a dilute amalgam, leaving copper in the solution. The amalgam thus obtained is then separated, heated at 350° in a stream of nitrogen to remove mercury, and gold in the residue is determined by the photometric *p*-dimethylaminobenzylidenerhodanine method.[3,5]

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Hirama model II photoelectric filter photometer with 1-cm cells (0·5–6 μg of gold).
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Standard gold solutions (5 μg *and* 0·4 μg *of gold per ml*): Dissolve pure gold foil in *aqua regia*, and dilute with 1*M* hydrochloric acid.
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4% (w/v) *Sodium chloride solution.*
1% *and* 0·5% (w/v) *Sodium fluoride solutions.*
Rhodanine solution: 0·003% *p*-dimethylaminobenzylidenerhodanine in absolute ethyl alcohol.
All of the reagents used were of reagent grade. Water purified by ion-exchange was used throughout the work.

Procedure

Separation of gold from copper and silver. Transfer a weighed sample (*a* g or less of copper metal) containing 0·1 to 6 μg of gold to a beaker of suitable capacity. Add a few ml of water and 4*a* ml of concentrated nitric acid, and heat to dissolve. Add 3*a* ml of concentrated hydrochloric acid, and continue heating for 10 min. Cool the solution, and add 20*a* ml of concentrated ammonia solution. Cool and dilute to 50*a* ml with water.

To this ammoniacal solution add a small amount of mercury (2 ml for 50 to 500 ml of the ammoniacal solution, 0·5 ml for 2·5 ml) and a stirring bar, cover the beaker, and stir the solution with a magnetic stirrer. Select the size and the rotating speed of the stirring bar so that numerous mercury globules (1 to 4 mm in diameter) may be formed. After the prescribed time (see *Results and Discussion*) stop stirring, discard the solution, and wash the mercury several times with water by decantation. Transfer the mercury to a 50-ml beaker, and remove moisture by blotting with a few pieces of filter paper. Transfer the mercury to a silica combustion boat, 90 by 20 mm and 10 mm deep, and evaporate the mercury at 350° in a stream of nitrogen, avoiding prolonged heating of the residue. Dissolve the residue in the boat in 2 drops of concentrated nitric acid and 1 drop of water with the aid of a glass rod, then add 3 drops of *aqua regia*.

If 0·5 to 6 μg of gold is present in the solution, transfer the latter to a 50-ml beaker, and rinse the boat with 2 drops of *aqua regia* and small portions of water to make the total volume in the beaker about 10 ml. Heat the solution for a few min, and cool to room temperature in the dark. Filter the solution through a small sintered-glass disk (No. 4), catching the filtrate in another 50-ml beaker, and wash with small portions of 0·01*M* hydrochloric acid.

If less than 0·5 μg of gold is present in the solution, transfer the latter to a 10-ml glass dish, and rinse the boat with 2 drops of *aqua regia* and small portions of water. Evaporate the solution to dryness on a water bath. Dissolve the residue in 4 drops of 1:1 *aqua regia*, and evaporate just to dryness on a water bath (70°). Dissolve the residue in 1 ml of 0·1*M* hydrochloric acid, heat on the water bath (70°) for 1 min, and cool to room temperature in the dark. Filter the solution through a small sintered-glass disk (No. 4), catching the filtrate in another 10-ml glass dish, and wash with eight portions of 0·1*M* hydrochloric acid of 0·5 ml each.

Photometric determination of 0·5 to 6 μg of gold. Evaporate the solution containing gold to dryness on a water bath, dissolve the residue in 1 to 5 drops of *aqua regia* and 0·5 ml of water, and evaporate just to dryness on the water bath (70°). Moisten the residue with 1 drop of concentrated hydrochloric acid, and again evaporate just to dryness on the water bath (70°). Add 2·5 ml of 0·12*M* hydrochloric acid and 5·0 ml of sodium chloride solution, heat for 5 to 10 min on the water bath, cool to room temperature, and add 0·50 ml of 1% sodium fluoride solution. Swirl the solution gently and add 0·50 ml of rhodanine solution dropwise. Transfer the solution to a 10-ml volumetric flask, dilute to the mark with water, and mix the solution by inverting the flask two or three times. Do not shake vigorously. After 15 to 20 min, measure the extinction of the solution in a 1-cm cell at 562 mμ against water. Determine the gold concentration by reference to a calibration curve prepared with the standard gold solution.

Photometric determination of 0·1 to 0·5 μg of gold. Evaporate the solution containing gold to dryness on a water bath, dissolve the residue in 2 drops of 1:1 aqua regia, and evaporate just to dryness on the water bath (70°). Moisten the residue with 1 drop of concentrated hydrochloric acid, and again evaporate just to dryness on the water bath (70°). Add 0·25 ml of 0·12*M* hydrochloric acid and 0·50 ml of sodium chloride solution, heat for 1 min on the water bath (70°), cool to room temperature, and add 0·10 ml of 0·5% sodium fluoride solution and 0·05 ml of rhodanine solution. Transfer the solution to a 1-ml volumetric flask, dilute to the mark with water, and mix the solution with the aid of a small polyethylene rod. After 15 to 20 min, measure the extinction of the solution in a 2-cm cell at 562 mμ against water. Determine the gold concentration by reference to a calibration curve prepared with the standard gold solution.

Tracer experiments

Radioactive gold was used in order to investigate the deposition rate and the over-all recovery of gold. A known amount of gold-198 solution was added to a copper solution, and the separation procedure described previously was carried out. Aliquots (1 or 2 ml) were taken from the ammoniacal solution during stirring with mercury and from the solution at completion of the entire separation step, and their activities were measured by means of a well-type scintillation counter.

RESULTS AND DISCUSSION

The deposition of gold into mercury globules from the ammoniacal solution was investigated as a function of time by the use of gold-198 as a tracer. Typical results are shown in Fig. 1. From these results, the following times were established for achieving essentially complete deposition of gold

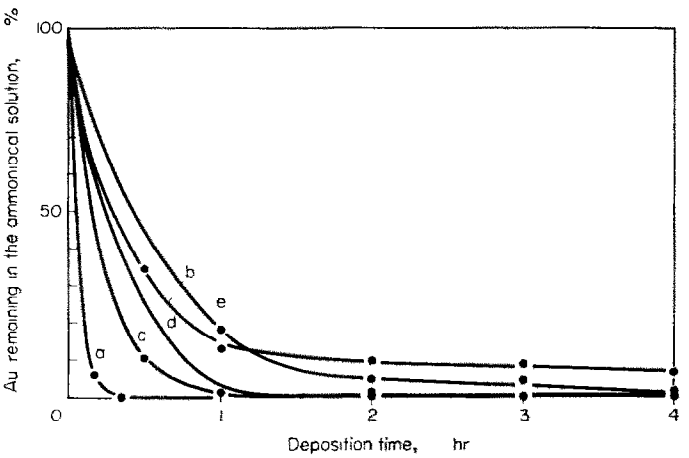


FIG. 1.—Deposition of gold into mercury globules from ammoniacal solution (mercury used: 2 ml):

(a) 50 ml of solution containing 5 μg of gold and 40 mg of copper,
(b) 50 ml of solution containing 5 μg of gold,
(c) 200 ml of solution containing 0·01 μg of gold and 40 μg of copper,
(d) 500 ml of solution containing 0·37 μg of gold, 60 μg of silver, and 10 g of copper,
(e) 500 ml of solution containing 0·24 μg of gold and 40 mg of copper.

from the solution containing copper; 1 hr for 50 ml or less of the ammoniacal solution, 2 hr for 200 ml, and 4 hr for 500 ml. However, if copper is absent from the solution, the deposition of gold is greatly retarded.

Synthetic solutions prepared from electrolytic copper (containing 0·013 ppm of gold and 6 ppm of silver), gold-198 and standard silver solutions, were analysed according to the procedure just given. The results shown in Table I indicate that gold in copper can be determined by this method within

TABLE I.—SEPARATION AND DETERMINATION OF GOLD IN SYNTHETIC SOLUTIONS

Exp. no.	Vol. of ammoniacal solution, *ml*	Present			Au found[a], *µg*	Au-198 recovered[b], %
		Cu, *g*	Ag, *µg*	Au, *µg*		
1	2·5	0·050	0	7·5	—	98
2	50	1·00	6	0·01	0·0	—
3	50	1·00	6	2·0	1·8	101
4	50	1·00	6	4·0	—	97
5	50	1·00	6	5·0	5·1	99
6	50	1·00	6	6·0	—	99
7	50	0·040	150	0·00	0·0	—
8	50	0·040	0	2·0	1·8	99
9	50	0·040	150	2·0	2·0	98
10	50	0·040	150	4·0	3·8	98
11	50	0·000	0	2·0	1·4	76
12	200	4·00	24	0·05	0·0	—
13	200	4·00	24	0·06	—	98
14	200	4·00	24	2·0	1·8	100
15	200	4·00	24	4·0	4·0	102
16	200	0·040	0	0·01	—	99
17	500	10·0	60	0·37	—	98
18	500	0·040	0	0·01	—	100

[a] By photometric procedure for 0·5 to 6 μg of gold.
[b] By radioactivity measurement (error, less than 2%).

an accuracy of 5% in the range of 1 to 100 ppm, and 10% at about 0·5 ppm. Less than 0·04 ppm of gold in copper can also be separated perfectly. Exp. 11 shows that the absence of copper from the ammoniacal solution results in an imperfect recovery of gold, in agreement with the results shown in Fig. 1. Therefore, a blank through the entire procedure was carried out after addition of a small amount (say 40 mg) of electrolytic copper to the solution. The blank value thus obtained corresponded to less than 0·01 μg of gold.

The calibration curve (concentration–extinction curve) in the photometric determination of gold is linear up to at least 0·6 ppm. The error is about 0·02 ppm in this range. No interference results from the presence of 100 ppm each of copper, iron and mercury; 5 ppm each of antimony, bismuth, cadmium, platinum and zinc; and 2 ppm of silver. However, even less than 0.5 ppm of palladium interferes with the determination of gold. In this experiment, all of the residues from the distillation of dilute amalgams had a weight of less than 0·5 mg, and no palladium was found in these residues by emission spectrographic analysis.

TABLE II.—DETERMINATION OF GOLD IN CRUDE AND ELECTROLYTIC COPPER

Sample	Sample taken	Vol. of ammoniacal solution, *ml*	Au found, *ppm*	
			Proposed method	Other methods
Crude copper I	36–54 mg	50	103, 96, 105, 105 (av.) 102	101[a]
	50 mg	2·5	100, 102, 98, 100 (av.) 100	95[b]
	3·2–4 mg	2·5	100, 102, 100 (av.) 101	95[c] (Ag 2762 ppm)
Crude copper II	48–72 mg	50	65, 68, 64 (av.) 66	64[a] 63[b] 69[c] (Ag 2269 ppm)
Crude copper III	160–220 mg	50	21, 22, 23 (av.) 22	22[a] 24[b] 23[c] (Ag 75 ppm)
Electrolytic copper	10 g	500	0·012, 0·013, 0·018[e], 0·010[f], (av.) 0·013	0·013[d] (Ag 6 ppm)

[a] Ion exchange-photometric method.
[b] Solvent extraction-photometric method.
[c] Dry assay.
[d] Ion exchange-neutron activation analysis.
[e] Sample analysed after addition of 0·10 μg of gold.
[f] Sample analysed after addition of 0·20 μg of gold.

The method was applied to the determination of gold in crude and electrolytic copper. The results are shown in Table II. In the case of crude copper, 3 to 5 g of the metal were dissolved in acids, and after settlement of small amounts of insoluble matter (silver chloride, silicates, *etc.*), an aliquot containing appropriate amounts of copper and gold was taken from the supernatant solution and analysed according to the procedure described previously. The results were in good agreement with those obtained by other methods of analysis.

Acknowledgement—The author wishes to thank Professor Shizo Hirano for his advice and encouragement.

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Summary—A new method of separation is described and applied to the determination of trace amounts of gold in copper metal. Gold is deposited into mercury globules from an ammoniacal solution of the copper. The resulting amalgam is heated to remove mercury, and gold in the residue is determined by the photometric *p*-dimethylaminobenzylidenerhodanine method. As little as 0.01 ppm of gold in copper can be separated and determined by the proposed method.

Zusammenfassung—Eine neue Trennungsmethode wird beschrieben, die am besten mit einer photometrischen Bestimmung von Goldspuren in Kupfermetall kombiniert wird. Gold wird aus ammoniakalischer Probelösung in Quecksilberkügelchen abgeschieden. Das Amalgam wird erhitzt und Gold im Rückstand mittels *p*-Dimethylaminobenzylidenrhodanin photometrisch bestimmt. Noch 0.01 ppm Gold können so abgetrennt und bestimmt werden.

Résumé—L'auteur décrit une nouvelle méthode de séparation et son application à la détermination spectrophotométrique des traces d'or dans le cuivre métallique. L'or est déposé dans des gouttelettes de mercure à partir de la solution ammoniacale de cuivre. L'amalgame ainsi formé est chauffé pour éliminer le mercure et l'or présent dans le résidu est dosé par spectrophotométrie en utilisant la p-diméthylaminobenzylidènerhodanine. Des quantités aussi faibles que 0,01 ppm d'or dans le cuivre peuvent être séparées et dosées par cette méthode.

REFERENCES

[1] E. B. Sandell, *Colorimetric Determination of Traces of Metals*. Interscience Publishers, Inc., New York, 3rd Ed., 1959. p. 494.
[2] W. E. Caldwell and K. N. McLeod, *Ind. Eng. Chem. Analyt.*, 1937, **9**, 530.
[3] S. Hirano, A. Mizuike and K. Yamada, *Japan Analyst*, 1960, **9**, 164.
[4] M. Shima, *Kagakukenkyusho-hokoku*, 1956, **32**, 152.
[5] S. Hara, *Japan Analyst*, 1958, **7**, 147.

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BOOK REVIEWS

Organic Analysis (in Hungarian). L. MÁZOR. Müszaki Könyvkiadó, Budapest, 1961, 286 pp. 26.50 Hungarian forint.

THIS book fills a long-felt gap in the Hungarian technical literature in which no summarising work on organic analysis has so far been published. Conscious of this, the author has endeavoured to make his book useful both for scientific research and as a university manual. The work is planned to be published in three volumes, the first of which, issued recently, discusses methods of organic qualitative analysis. It deals with methods of preliminary testing and of qualitative elementary analysis. It also discusses the determination of physical constants, and considers the systematic qualitative analysis of organic compounds and their mixtures, as well as methods suitable for determining characteristic groups. It deals briefly with the application of ultraviolet and infrared spectrophotometry. Ways of compiling and utilising literature data are discussed and a method for producing derivatives is included.

The well-systematised, explicit text is completed by illustrative figures and tables. With the aid of these any reader possessed of elementary chemical knowledge, should find the best way for testing organic compounds.

ÉVA GÖRÖG

Quantitative Chemistry. A Laboratory Text. JURG WASER. W. A. Benjamin, Inc., Publishers, New York, U.S.A. Pp. 286. $3.25.

THE chief purpose of this book is to provide a laboratory text for a course in general and quantitative chemistry. A secondary objective is its use in any first course in quantitative chemistry.

Essentially, the text is a good quantitative analysis laboratory manual, featuring an expanded explanation of the principles and techniques used in each experiment. Many of these details are very worthwhile, but some of the explanations seem a bit too lengthy.

Twelve diverse type of experiments are described. These range from simple gravimetric chloride and acid-base titrations up through rather complicated coulometric analysis and the method of continuous variation. Most of the experiments are typical of those in a regular quantitative analysis course. However, several of the more advanced experiments could be classified as "instrumental methods". These should prove to be quite challenging for beginning students.

As a quantitative analysis laboratory text it is to be recommended. However, a great deal of the material seems beyond the capabilities of the usual freshman class. Its use at the freshman level should probably be restricted to talented groups.

F. H. FIRSCHING

Proceedings of the Second International Symposium on Enzymes in Clinical Chemistry (held at Ghent, Belgium in April, 1961). Butterworth, London, 1962. pp. 130. 60s.

THIS book, which appeared originally as numbers 3–4 of Pure and Applied Chemistry, Volume 3, comprises sixteen papers on a subject of rapidly growing importance and application. It would have been helpful if the reprint could have included English summaries to the French and German contributions; and the omission of the Symposium discussions is disappointing. Nevertheless, those concerned with the use of enzymatic techniques, whether in clinical medicine or biochemical research, will find much here to guide and stimulate.

There are a few papers dealing primarily with technique of assay but most are concerned with the measurement of enzyme concentrations in normal and pathological fluids and tissues as a guide to clinical diagnosis. In this respect, the papers describing studies of isoenzymes are of particular interest. As the work of F. Wroblewski indicates, it is obvious that such "diagnostic dissection" by use of starch-gel electrophoresis, *etc.* is going to find wide application in clinical laboratories. The author

Talanta, 1962, Vol. 9, pp. 953 to 954. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEWS

Organic Analysis (in Hungarian). L. MÁZOR. Müszaki Könyvkiadó, Budapest, 1961, 286 pp. 26.50 Hungarian forint.

THIS book fills a long-felt gap in the Hungarian technical literature in which no summarising work on organic analysis has so far been published. Conscious of this, the author has endeavoured to make his book useful both for scientific research and as a university manual. The work is planned to be published in three volumes, the first of which, issued recently, discusses methods of organic qualitative analysis. It deals with methods of preliminary testing and of qualitative elementary analysis. It also discusses the determination of physical constants, and considers the systematic qualitative analysis of organic compounds and their mixtures, as well as methods suitable for determining characteristic groups. It deals briefly with the application of ultraviolet and infrared spectrophotometry. Ways of compiling and utilising literature data are discussed and a method for producing derivatives is included.

The well-systematised, explicit text is completed by illustrative figures and tables. With the aid of these any reader possessed of elementary chemical knowledge, should find the best way for testing organic compounds.

ÉVA GÖRÖG

Quantitative Chemistry. A Laboratory Text. JURG WASER. W. A. Benjamin, Inc., Publishers, New York, U.S.A. Pp. 286. $3.25.

THE chief purpose of this book is to provide a laboratory text for a course in general and quantitative chemistry. A secondary objective is its use in any first course in quantitative chemistry.

Essentially, the text is a good quantitative analysis laboratory manual, featuring an expanded explanation of the principles and techniques used in each experiment. Many of these details are very worthwhile, but some of the explanations seem a bit too lengthy.

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shows, for instance, that the isoenzyme pattern of plasma lactic dehydrogenase observed during the course of myocardial infarction provides a more reliable parameter of myocardial necrosis than does the measurement of *total* serum or plasma enzyme activity.

Other studies are concerned with the origin of tissue enzymes and the effect of activators, whilst one group has employed enzyme tests to measure the concentration of toxic intermediate metabolites in various diseases.

It seems probable that the price of this book will encourage readers to make use of the original publication of the Proceedings, which also has the advantage of a subject index.

D. R. STANWORTH

Talanta, 1962, Vol. 9, p. 955. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

(Material for this section should be sent directly to the Associate Editor)

UNITED KINGDOM

Wednesday 7 *November* 1962: **Fluoride, Teeth and the Analyst:** Dr. H. J. CLULEY, Dr. J. LONGWELL and Dr. N. JENKINS: *Society for Analytical Chemistry.* The Wellcome Building, Euston Road, London, N.W.1.

Thursday 8 *November* 1962: **Solvent Extraction:** Dr. T. B. PIERCE: *Society for Analytical Chemistry, Midlands Section.* Technical College, Nottingham.

Friday 9 *November* 1962: **Some Organic Applications of Polarography:** *Polarographic Society.* College of Advanced Technology, Loughborough.

Monday 12 *November* 1962: **Solvent Extraction of Inorganic Compounds. Some Recent Developments:** Professor H. M. N. H. IRVING. *Society for Analytical Chemistry, North of England Section* and *Tees-side Section of the Royal Institute of Chemistry.* Constantine Technical College, Middlesbrough.

Tuesday 27 *November* 1962: **Recent Improvements in Separation Techniques:** Professor H. M. N. H. IRVING and Dr. D. GROSS. *Society for Analytical Chemistry, Physical Methods Group.* The Chemical Society, Burlington House, London, W.1.

Wednesday 5 *December* 1962: **Applications of X-Ray Fluorescence:** Mr. R. G. STONE, Mr. R. F. SERMIN and Dr. E. T. HALL: *Society for Analytical Chemistry* with *Physical Methods Group.* The Chemical Society, Burlington House, London, W.1.

Saturday 8 *December* 1962: **Nuclear Magnetic Resonance:** Professor E. R. ANDREW. *Society for Analytical Chemistry, North of England Section* and *Physical Methods Group.* Old Nag's Head Hotel, Lloyd Street, Manchester.

Friday 14 *December* 1962: **The Determination of Carbon and Hydrogen in Organic Materials:** Dr. A. M. G. MACDONALD: *Society for Analytical Chemistry, Midlands Section* and *Microchemistry Group.* The University, Birmingham 15.

Wednesday 10 *July—Wednesday* 17 *July* 1963: **XIXth International Congress of Pure and Applied Chemistry:** London. The Congress will be organised into divisions for Organic, Inorganic, Analytical and Applied Chemistry. The Analytical Chemistry division will include the following sections:

1—*Trace Analysis.*

2—*Separation Methods.*

3—*Electroanalysis.*

4—*Teaching of Analytical Chemistry.*

Copies of the second congress circular are now available, and may be obtained from the Honorary Secretary, XIXth International Congress of Pure and Applied Chemistry, 14 Belgrave Square, London, S.W.1. The final date for applications to read papers and for submission of abstracts for the Congress is *Monday* 21 *January* 1963.

Friday 9–*Thursday* 15 *August* 1963: **6th International Congress of Nutrition, Edinburgh, Scotland.** This will include a session on **Isotopes in Nutritional Investigations.** Further information may be obtained from Miss A. D. WATSON, Hon, Organising Secretary, 6th International Congress of Nutrition, Clinical Chemistry Department, Royal Infirmary, Edinburgh, 3, Scotland.

UNITED STATES OF AMERICA

Monday 33–*Thursday* 7 *February* 1964: **International Conference on Materials:** American Society *for Testing and Materials* and *International Union of Testing and Research Laboratories for Materials and Structures:* Sheraton Hotel, Philadelphia, Pa. Emphasis will be laid on materials technology, on world standardisation, and on the use of nuclear physics in the testing of materials. Further information may be obtained from H. H. HAMILTON, Public Relations, American Society for Testing and Materials, 1916 Race Street, Philadelphia 3, Pa.

Talanta, 1962, Vol. 9, p. 956. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Ion-exchange study of thiocyanatochloro complexes of rare earth elements: H. HAMAGUCHI, R. KURODA and N. ONUMA (27 *August* 1962).

The determination of small amounts of calcium in the presence of large amounts of alkali metal salts by amperometric chelatometry: M. L. RICHARDSON (28 *August* 1962).

Extraction of the cupferron complex of niobium: JAMES F. REED (30 *August* 1962).

Nephelometric examination of barium sulphate precipitation: A. G. WALTON and T. HLABSE (5 *September* 1962).

Precipitation of metal 8-hydroxyquinolates from homogeneous solution—VI: Zinc: J. P. JONES, O. E. HILEMAN JR., and L. GORDON (5 *September* 1962).

The determination of oxidising and reducing cations in transition-metal oxides using vanadium sulphate solutions: D. G. WICKHAM and E. R. WHIPPLE (5 *September* 1962).

Coprecipitation with uranous oxalate: JACOB BLOCK and LOUIS GORDON (5 *September* 1962).

Elimination of anionic interferences in the flame spectrophotometric determination of calcium: Use of glycerol as a releasing agent: T. C. RAINS, H. E. ZITTEL and MARION FERGUSON (7 *September* 1962).

Micro determination of the neutralisation equivalents of higher fatty acids by non-aqueous titrations: R. D. TIWARI and J. P. SHARMA (10 *September* 1962).

Untersuchung der Kationensorption aus Komplexanmedium—IV: Trennung von Calcium und Magnesium aus Lösungen von Athylengly-kol-bis-(β aminoäthyläther)-N,N′-tetraessigsäure: PAVEL POVONDAR and RUDOLF PRIBIL (10 *September* 1962).

Contribution to the basic problems of complexometry—XII: Determination of aluminium in the presence of iron and titanium: RUDOLF PŘIBIL and VLADIMIR VESELÝ (10 *September* 1962).

The determination of microgram quantities of zirconium in iron, cobalt and nickel alloys by X-ray fluorescence: OWEN H. KRIEGE and JOSEPH S. RUDOLPH (10 *September* 1962).

Comparison of solvents for the differentiating titration of phenols: N. T. CRABB and F. E. CRITCHFIELD (17 *September* 1962).

Determination of thorium in granite by gamma spectrometry and by radiotracer: S. A. REYNOLDS (17 *September* 1962).

A nomogram for acid-base titrations: E. WANNINEN (17 *September* 1962).

Determination of gold-platinum-palladium-nickel and gold-palladium-rhodium-ruthenium in mixtures using ring colorimetry: E. J. SINGH and ARUN K. DEY (24 *September* 1962).

Arsenic in glass: J. A. RYAN and J. R. SANDERSON (10 *September* 1962).

Estimation of the hydrogen content of palladium and palladium alloys from measurements of electrode potential and electrical resistance: J. C. BARTON and F. A. LEWIS (28 *September* 1962).

Isotopic dilution analysis by solvent extraction—V: Determination of traces of iron: JIŘÍ STARÝ, JAROMÍR RŮŽIČKA and MILAN SALAMON (28 *September* 1962).

The determination of traces of selenium and tellurium in samples of platinum by neutron-activation analysis: D. F. C. MORRIS and R. A. KILLICK (28 *September* 1962).

Talanta, 1962, Vol. 9, pp. 957 to 985. Pergamon Press Ltd. Printed in Northern Ireland

ION EXCHANGE IN MIXED SOLVENTS

ADSORPTION BEHAVIOUR OF URANIUM AND THORIUM ON STRONG-BASE ANION-EXCHANGE RESINS FROM MINERAL ACID–ALCOHOL MEDIA
SEPARATION METHODS FOR URANIUM AND THORIUM

J. KORKISCH and G. E. JANAUER
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(*Received* 1 *January* 1962. *Revised* 5 *April* 1962. *Accepted* 5 *May* 1962)

Summary—The present work summarises important data hitherto reported on the anion-exchange behaviour of uranium^{VI} and thorium^{IV} in mixed solvents, and the results of pertinent research work carried out in this laboratory. The purpose of this paper is to give a detailed description of the adsorption behaviour of these actinide elements on strong-base anion-exchange resins in mineral acid solutions containing aliphatic alcohols. Equilibrium studies show the distribution coefficients to vary greatly with the acid used, as is expected from the results earlier obtained in aqueous systems. In mixtures of a given mineral acid with different alcohols, the distribution coefficients depend on the alcohol percentage, as well as on the acidity of the solutions, and on the dielectric constants and chain lengths of the alcohols employed. The results of these investigations can be applied to the separation of thorium and uranium from each other and from practically all other cations and anions. Two of the separation methods developed have already found general application for the assay of uranium and thorium in materials of greatly varying composition. Finally, the general theoretical aspects of anion exchange in mixed solvents are discussed, and the results obtained for uranium and thorium are interpreted accordingly.

1. INTRODUCTION

THE anion-exchange properties of uranium^{VI} and thorium^{IV} in aqueous mineral acid solutions in the presence of a strong-base anion exchanger have been a subject of extensive investigations by many authors. Kraus and collaborators,[1–5] who can be regarded as pioneers in this field, have presented the first comprehensive studies on the distribution of nearly all elements, including thorium and uranium, between strong-base anion exchangers and mineral acids, especially hydrochloric acid. Their work has been confirmed and extended by Bunney, Ballou, Pascual and Foti[6] and others.[7–12] The adsorption of uranium and thorium on strongly basic resins from nitric acid solutions has been studied in detail by Buchanan and Faris,[13] Carswell,[14] Danon[15–16] and Ying-Mao Chen *et al.*[17] and others.[18–19] Jenkins and Richardson[20] as well as Saito and Sekine[21] proved the anionic character of uranium and thorium in nitrate and sulphate solutions.

Based on all these results numerous useful separation methods for uranium have been developed in hydrochloric,[3,22–27] nitric[14–16,28–30] and sulphuric[4,31–53] acid media, and are being extensively applied in the analysis of ores, rocks and various other materials. In addition, other strong and weak acids and complexing agents for uranium, such as hydrochloric-hydrofluoric-acid mixtures,[4,54] phosphoric acid,[55–57] carbonate,[58] acetate,[59–61] and ascorbinate[62–64] have been examined and found to be

applicable for the isolation and separation of uranium. The anion-exchange properties of thorium, on the other hand, have found but little application and the methods developed are restricted mainly to ascorbic acid,[63–64] EDTA-solutions,[65–68] nitric[13,19] and sulphuric[69] acid solutions of this element.

In contrast to the systematic work done on ion exchange in pure aqueous acidic systems, few efforts have been made to cover the vast field of organic solvents systematically in respect of their influence on the anion-exchange behaviour of elements in different mineral acid solutions. Fritz and Pietrzyk[70] determined the distribution coefficients of many metal ions, including thorium and uranium, between the strong-base anion exchanger Dowex 1 and mixtures of methanol, ethanol and isopropanol, with varying contents of hydrochloric acid of different normalities. A number of successful column separations of metal ion mixtures were developed by these authors. Beside the authors cited by Fritz and Pietrzyk,[70] Katzin and Gebert,[71] Davies and Owen,[72] Tuck and Welch,[73] Iguchi,[74,75] Burstall *et al*[76], Berg and Truemper,[77] Kojima[78,79] and Yoshino and Kurimura[80] there are a few more who have published on the subject of anion exchange in non-aqueous and mixed solvents. Recently Janauer and Korkisch[81] have studied the anion-exchange behaviour of vanadium in hydrochloric acid solutions of the aliphatic alcohols; and a method for the separation of vanadium and nickel from iron and copper was developed. This separation method proved to be suitable for the determination of vanadium and nickel in ashes of oil products.[82] Samuelson and Sjöström[83] used 60% ethanol as an eluent for the alkali metals from a column of Dowex 2 loaded with EDTA. When separation of transition elements was desired (Samuelson, Sjöström and Forsblom[84]) the elution of the alkali metals was performed with 50% ethanol, the column containing acetate or oxalate or citrate instead of EDTA. Edge[85,86] studied the anion-exchange behaviour of yttrium, neodymium and lanthanum in dilute nitric and hydrochloric acid solutions containing ethanol, and found that these three rare earth elements could not be resolved by any of the ethanol-hydrochloric acid eluent systems employed. Elution with 0·8*N* nitric acid-80% ethanol or 1·6*N* nitric acid-80% ethanol appeared to be suitable for preparing "light" and "heavy" concentrates from mixtures of rare earth elements. Katzin and Sullivan[87] have invented a process utilising the strongly basic exchangers Dowex 1 and 2 for the separation of inorganic salts from their solutions in oxygen-containing organic solvents mixed with hydrochloric or nitric acid. The main object of this process is the separation of uranium^{VI} and/or plutonium^{IV} from organic solutions and/or uranium from thorium. Among other solvents, acetone and hexone were used. Very interesting results have also been obtained by the study of cation exchange in acetone-mineral acid mixtures, as, for instance, by Kember *et al.*,[88] who developed a useful method for the separation of copper and nickel using acetone containing 4% hydrochloric acid and 10% water as the eluent. Other cation-exchange methods in non-aqueous and mixed solvents have been reviewed by Bonner.[89]

From a close survey of all the literature available on anion exchange in non-aqueous or mixed solvents it appears that information on the exchange behaviour of uranium and thorium in such media is still scanty,[70,87*] and no class of organic solvents has as yet been systematically investigated.

* The methods for the isolation of uranium and thorium described by Korkisch *et al*[99,100] (see also page 959) have been the first in which ion exchange in mixed solvents was applied to separate these two radioelements from a number of foreign elements.

For this reason, a long-term research programme was initiated at this Institution which has, since 1960, been continued in close co-operation with the International Atomic Energy Agency and the U.S. Atomic Energy Commission.[90,91] Part of this research was devoted to a systematic investigation of the aliphatic alcohols* with regard to their influence on the adsorption of uranium and thorium from mixtures with mineral acids on strongly basic anion-exchange resins of the quaternary amine type. The systems hydrochloric acid-ROH, nitric acid-ROH and sulphuric acid-ROH were completely covered,[90–98] and the condensed results and a number of the most important applications[64,96,97,99–103] based on these findings are presented in this paper, and compared with relevant results published by other research teams.

2. EXPERIMENTAL PART

I. *Reagents*

(a) *Ion-exchange resins:* The most usual was the strongly basic anion exchanger Dowex 1, ×8 (100–200 mesh, occasionally also 50–100 mesh chloride form).[90–98]

For the experiments in nitric and sulphuric acid solutions, the resin was transformed into the nitrate or sulphate form. After preparation of the sulphate form, prolonged washing is necessary, since free sulphuric acid adheres very strongly to the resin.[104] The air-dried form of the nitrate or the sulphate form of this resin was employed. In a few cases the strongly basic anion exchanger Amberlite IRA-400 (50–100 mesh, chloride form) was also used.

(b) *Standard solutions of uranium and thorium:* Hydrochloric, nitric, and sulphuric acid solutions of uranyl and thorium chlorides, nitrates, and sulphates of exactly known acidity and uranium[105] and thorium[106] content were employed.[90–98]

(c) *Solvents:* The aliphatic alcohols employed (methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol and a mixture of the amyl alcohols) were reagent-grade solvents.[90–98] All hydrochloric, nitric, and sulphuric acid solutions needed were prepared from their reagent-grade concentrated acids.

(d) *Solutions of other elements:* Standard solutions of a great number of elements were prepared from their reagent-grade salts. They were mainly employed for checking the possibilities of separating these elements from uranium and thorium. Their standardisation and quantitative determination has been described earlier.[64,81,96,99–103]

(e) *Dyestuff solutions:* 0·1% aqueous solution of thoronol.[106] The preparation of Solochromate Fast Red solutions and those of other dyestuffs of the Solochrome class which have also been used for spectrophotometric determination of uranium and thorium has already been described elsewhere.[107]

(f) *Other reagents:* Ascorbic acid; pure product (Wiener Heilmittelwerke). Hydrofluoric acid; 38–40% reagent grade. Perhydrol; 30% hydrogen peroxide, reagent grade.

II. *Apparatus*

(a) *Ion-exchange columns:* The column operations were carried out in columns of the same type and dimensions as described earlier.[29,59,62,90–98]

(b) *Spectrophotometer:* For the spectrophotometric determination of thorium and greater amounts of uranium the Beckman model B and DU spectrophotometers were employed. The measurements were carried out at wavelengths of 545 mμ (thorium-thoronol[106]) and 490 mμ (thorium or uranium-Solochromate Fast Red[107]) using 1-cm cells and a blue-sensitive phototube.

(c) *Polarographs:* For the quantitative determination of uranium by means of the catalytic nitrate wave, the polarographs Sargent, model XII and Metrohm-Polarecord type E,261 R were employed. The exact conditions of measurements and the evaluation of the polarograms has been described earlier.[59,60,61]

(d) *Fluorimeter:* Very small amounts of uranium were determined fluorimetrically using a procedure described by Schönfeld, El Garhy, Friedmann and Veselsky.[108] The photoelectric fluorimeter employed was a Galvanek Morrison Fluorimeter, Mark V.

III. *Determination of distribution coefficients*

The distribution coefficient for uranium or thorium is defined by the following equation:

$$\text{Distribution coefficient} = K_d = \frac{\mu\text{g of uranium or thorium/g of resin}}{\mu\text{g of uranium or thorium/ml of solution}},$$

* Other solvents as instance ethers and ketones, are being investigated in the course of these studies.

and was determined employing the batch equilibrium method (batch method).[90-98] In the case of higher alcohols like n-butanol, isobutanol and amyl alcohol, which are partly miscible with water, the distribution coefficients can only be determined at very high percentages of these alcohols; that is, if the ratio of aqueous phase to alcoholic phase is 1:10 or lower. This ratio, however, can be 1:5 or above if hydrochloric acid-alcohol mixtures are employed, because the miscibility in such media is much higher than in nitric- or sulphuric acid mixtures.

All measurements of the distribution coefficients were performed disregarding any changes from mixing in preparing the acid-alcohol mixtures.

IV. *Determination of exchange capacities (Effect of concentration on the distribution coefficients)*

The capacity of the resin for uranium or thorium under certain experimental conditions was determined by measuring the distribution coefficients at different steadily increasing uranium or thorium concentrations under identical conditions. The maximal exchange capacity thus obtained corresponds to complete saturation of the resin with the uranium or thorium complex in question. The results of these measurements are given on page 972 (Section 3). The chloride, nitrate, and sulphate capacity of the resin was found to be 3·4 ± 0·05 mg equiv./g of air dried resin.

V. *Column operations*

The column operations pertaining to the individual separation methods (see Tables I–III) were performed in the manner described earlier[90-98].

VI. *Quantitative determination of uranium and thorium*

(*a*) *Determination of uranium:* The quantitative determination of uranium in the eluates or filtrates (after removal of the resin by filtration) was performed polarographically, as has earlier been described.[59,90-98] This method allows the exact determination of 0·1–20 μg of uranium in 10 ml of solution. For the determination of higher amounts of uranium a spectrophotometric method using Solochromate Fast Red[107] was used. Amounts of uranium below 0·1 μg were determined fluorimetrically.[108]

(*b*) *Determination of thorium:* For the quantitative determination of thorium, thoronol was employed as the photometric reagent.[95,97,99]

3. RESULTS

I. *Effect of Alcohol Concentration on the Adsorption of Uranium and Thorium*

1. *In hydrochloric acid-alcohol mixtures*

The results are shown in Figs. 1a and 1b.

Discussion

Fig. 1*a*: From the curves it is seen that uranium adsorption increases with the alcohol concentration and also with the chain length of the alcohols (see also Fig. 4). The increase is more marked at higher alcohol concentrations. As will be shown later, there is also a relationship between the increase of the distribution coefficients and dielectric constants of the alcohols used (see Fig. 5). In order to simplify the recording of the results, the individual values of the distribution coefficients obtained in amyl alcohol mixtures are not shown as a curve but only as single points and for the same reason, the results obtained in isopropanol and isobutanol are recorded in Table I. From these results it may be seen that the uranium adsorption from such mixtures is lower than that from media containing the corresponding n-alcohols (compare values from Table I with Fig. 1a).

Fig. 1*b:* This figure shows that the distribution coefficients for thorium also increase with increasing concentration and chain length of the alcohols employed (compare with Fig. 4). The effect of the chain length of the alcohols is, however, only noticeable with the short chain alcohols, *i.e.*, methanol and ethanol, in comparison with

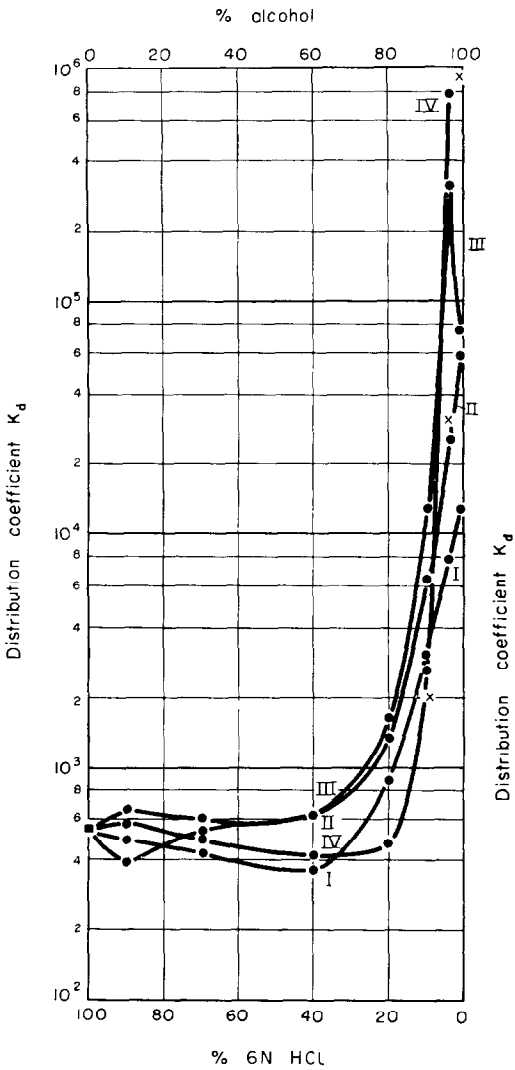


FIG. 1a.—Effect of alcohol concentration on the adsorption of uranium on Dowex 1 from hydrochloric acid-alcohol mixtures
I—Methanol; II—Ethanol; III—n-Propanol; IV—n-Butanol; ×—Amyl alcohol; ■—Kraus and Nelson[2] (Dowex 1)

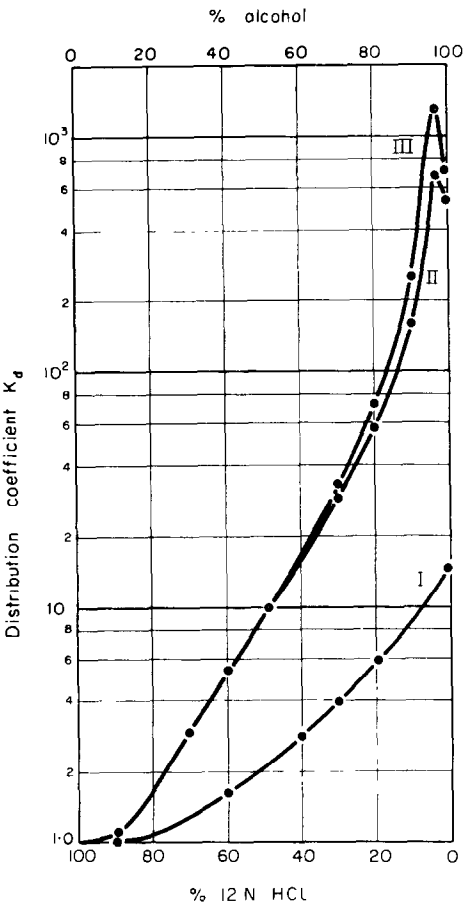


FIG. 1b.—Effect of alcohol concentration on the adsorption of thorium on Amberlite IRA 400 from hydrochloric acid-alcohol mixtures
I—Methanol; II—Ethanol; III—n-Propanol, Isopropanol, n-Butanol and Amyl alcohol

TABLE I. URANIUM ADSORPTION FROM ISOPROPANOL AND ISOBUTANOL-HYDROCHLORIC ACID MIXTURES

Alcohol, %	K_d in isopropanol-HCl	K_d in isobutanol-HCl
99	$2{\cdot}5 \times 10^5$	$2{\cdot}2 \times 10^5$
96	$4{\cdot}2 \times 10^5$	$1{\cdot}5 \times 10^5$
90	$1{\cdot}35 \times 10^5$	$4{\cdot}14 \times 10^3$
80	$9{\cdot}98 \times 10^3$	$1{\cdot}64 \times 10^3$
60	$1{\cdot}12 \times 10^3$	$5{\cdot}8 \times 10^2$
30	$7{\cdot}8 \times 10^2$	$4{\cdot}8 \times 10^2$
10	$5{\cdot}6 \times 10^2$	$4{\cdot}8 \times 10^2$

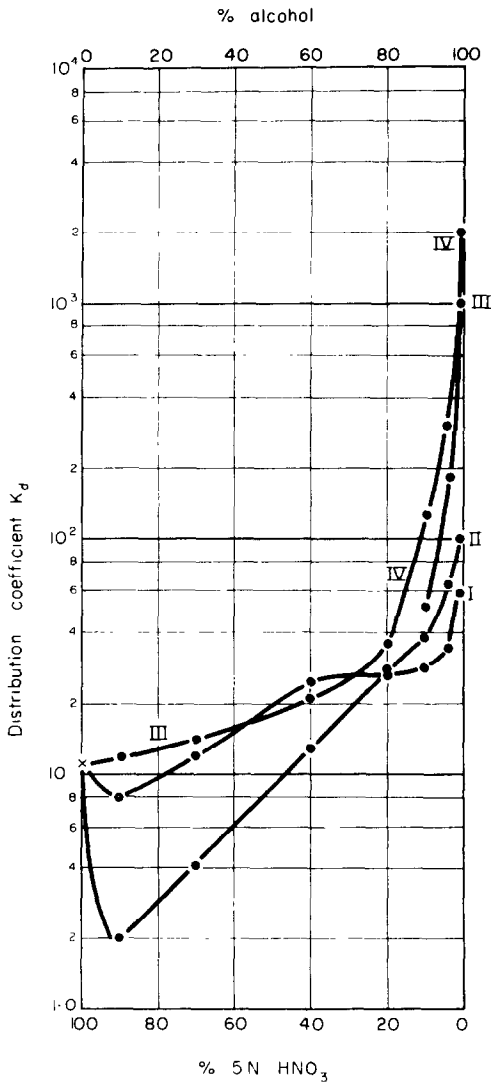


FIG. 2a.—Effect of alcohol concentration of the adsorption of uranium on Dowex 1 from nitric acid-alcohol mixtures
I—Methanol; II—Ethanol; III—n-Propanol; IV—n-Butanol, Isobutanol, Amyl alcohol,
×—Buchanan and Faris[13] (Dowex 2)

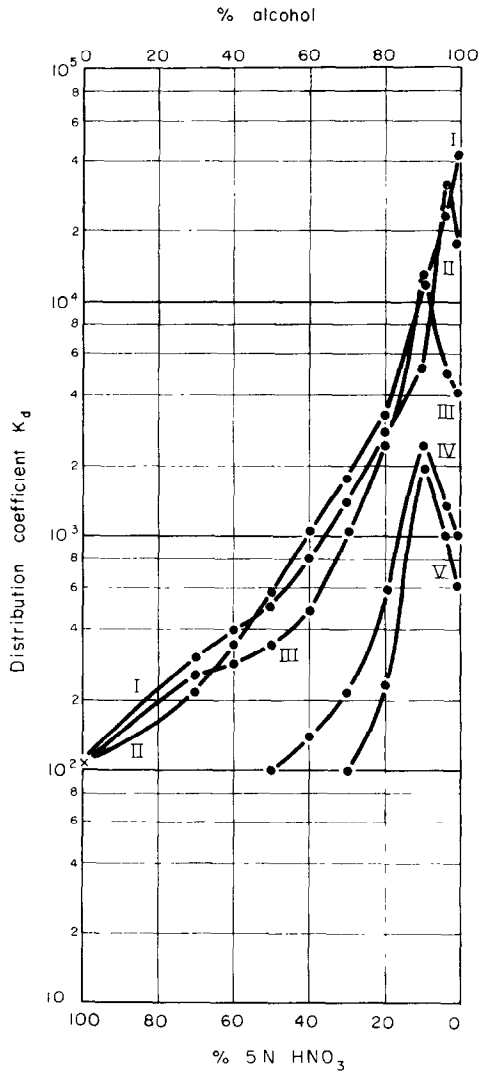


FIG. 2b.—Effect of alcohol concentration on the adsorption of thorium on Dowex 1 from nitric acid-alcohol mixtures
I—Methanol; II—Ethanol; III—n-Propanol; IV—n-Butanol; V—Amyl alcohol;
×—Buchanan and Faris[13] ((Dowex 2)

the longer chain alcohols propanol, butanol and amyl alcohol, in the mixtures of which identical distribution coefficients were obtained (see also Fig. 4).

In conclusion, it may be said that uranium and thorium can be adsorbed from mixtures of the longer-chain alcohols at high percentages of these alcohols, although the distribution coefficients differ considerably. However, the absolute values of the distribution coefficients in those systems are still high enough to ensure quantitative adsorption of both elements. Thus the simultaneous adsorption of uranium and

thorium can be accomplished in such media, although it is impossible in pure aqueous hydrochloric acid solutions, as shown by Kraus and collaborators.[1–5]

2. *In nitric acid-alcohol mixtures*

The results of these investigations are given in Figs. 2a and 2b.

Discussion

Fig. 2a: From this figure it is evident that the adsorption of the uranyl nitrate complex is strongest from butanol and amyl alcohol media, and weakest from methanol medium; and this effect is also accentuated with increasing alcohol concentration. In addition, the distribution coefficient increases with increasing chain length (see also Fig. 4), but the regularity is interrupted at lower percentages of alcohol in the mixtures, a result which might possibly be caused by partial esterification.

Fig. 2b: The results recorded in these curves make it apparent that reverse conditions are encountered with thorium from those with uranium under identical experimental conditions. The thorium nitrate complex is most strongly adsorbed from methanol, and is only weakly adsorbed from amyl alcohol medium. The adsorption of thorium decreases with increasing chain length of the alcohols (see also Fig. 4). Secondary alcohols like isopropanol and isobutanol show the same behaviour as the corresponding straight-chain alcohols.

3. *In sulphuric acid-alcohol mixtures*

The results of these experiments are recorded in Fig. 3a and 3b.

Discussion

Fig. 3a: It is seen that the distribution coefficient of uranium in sulphuric acid–alcohol mixtures also rises with increasing alcohol concentration, but not with increasing chain length (see also Fig. 4). Very high values for the distribution coefficients are reached at high alcohol concentrations, independent of the chain length of the alcohols used.

Fig. 3b: The distribution coefficient of thorium shows the same behaviour as that of uranium *i.e.*, it also rises with increasing alcohol concentration independent of the alcohol chain length (see Fig. 4). The curve in Fig. 3b therefore shows the adsorption coefficients for thorium in all the alcohols investigated.

II. *Effect of Chain Length and Dielectric Constant of Alcohols on the Distribution Coefficients of Uranium and Thorium*

1. *Effect of chain length*

To illustrate the effect of the chain length of the alcohols on the distribution coefficients of uranium and thorium, the distribution coefficients were plotted against the number of carbon atoms (see Fig. 4). (For every curve the experimental conditions such as over-all acidity and alcohol concentration were kept constant).

As can be seen from curves I and II of this figure, the increase of chain length produces a steep increase of the distribution coefficients of uranium and thorium in hydrochloric acid-alcohol media, as has earlier been observed[81] with vanadium^{IV} and vanadium^{V}. In nitric acid-alcohol media, uranium also shows an increase of K_d

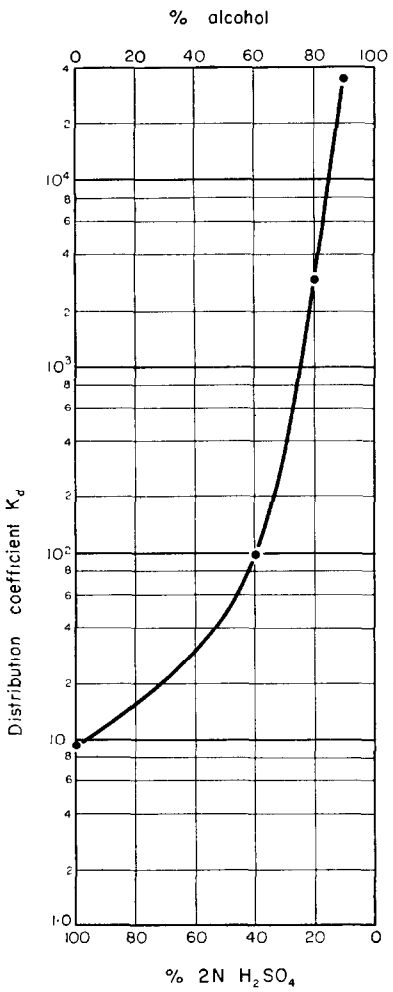


FIG. 3a.—Effect of alcohol concentration on the adsorption of uranium on Dowex 1 from sulphuric acid-alcohol mixtures

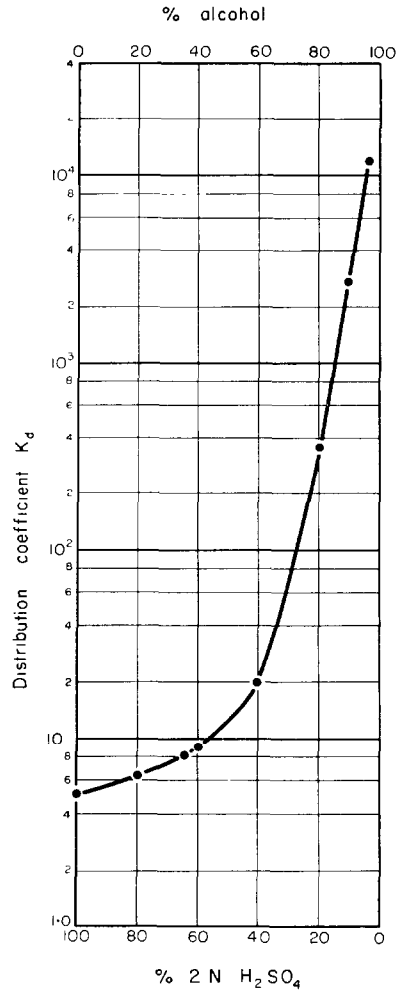


FIG. 3b.—Effect of alcohol concentration on the absorption of thorium on Dowex 1 from sulphuric acid-alcohol mixtures

while the distribution coefficient of thorium falls off rather rapidly with increasing number of carbon atoms. In sulphuric acid-alcohol mixtures no effect of chain length whatsoever was found. As the change of K_d caused by the increase of carbon atoms from 4 to 5 is rather small in nitric and hydrochloric acid media, we have neglected the fact that amyl alcohol is not a pure n-alcohol, but a mixture of some isomers.

2. *Effect of dielectric constant*

To show the effect of the dielectric constant (DC) of the alcohols and water on the adsorbability of uranium and thorium on strong-base anion exchangers from mineral acid-alcohol solutions, we have plotted the K_d values against $\frac{1 \times 10^2}{D.C}$ (20°) of the pure alcohols, neglecting the influence of the small water content [alcohol percentages were 99% or 90% (see Fig. 5) in the mixtures].

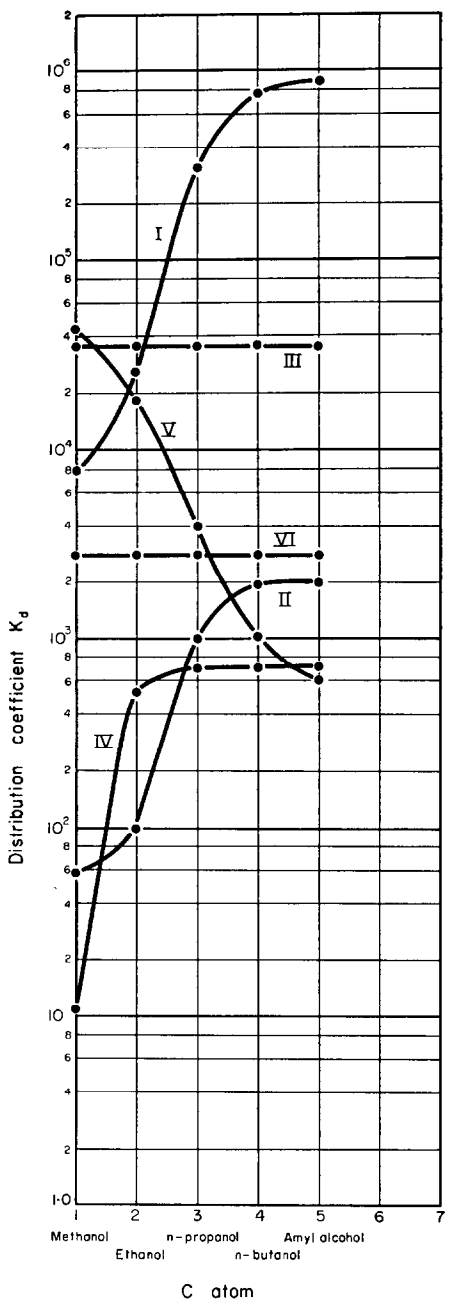


FIG. 4.—Effect of chain length
I—Uranium; 96% alcohol, 4% 6*N* HCl;
II—Uranium; 99% alcohol, 1% 5*N* HNO_3:
III—Uranium; 90% alcohol, 10% 2*N* H_2SO_4:
IV—Thorium; 99% alcohol, 1% 12*N* HCl:
V—Thorium; 99% alcohol, 1% 5*N* HNO_3:
VI—Thorium; 90% alcohol, 10%2*N* H_2SO_4.

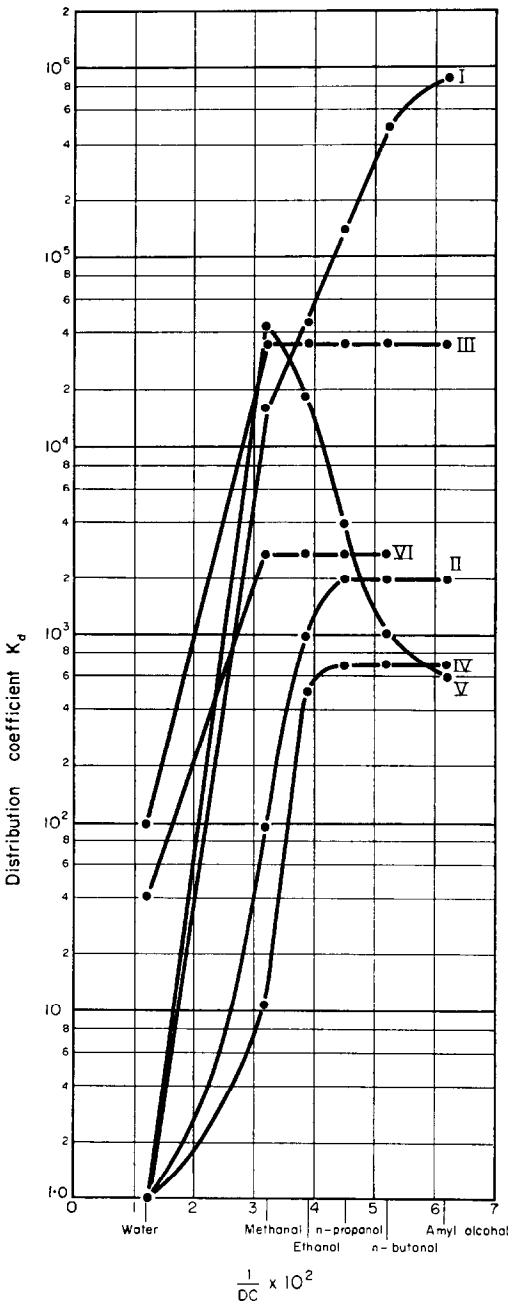


FIG. 5.—Effect of dielectric constant
I—Uranium; 99% alcohol or water, 1% 6*N* HCl:
II—Uranium; 99% alcohol or water, 1% 5*N* HNO_3: III—Uranium; 90% alcohol or water, 10% 2*N* H_2SO_4: IV—Thorium; 99% alcohol or water, 1% 12*N* HCl: V—Thorium; 99% alcohol or water, 1% 5*N* HNO_3: VI-Thorium; 99% alcohol or water, 1% 2*N* H_2SO_4.

Comparison with Fig. 4 shows a very similar relationship between both the effects of chain length and dielectric constant and the adsorption of uranium and thorium; that is, increasing adsorption with decreasing DC of both uranium and thorium in hydrochloric acid-alcohol media and for uranium in nitric acid-alcohol media. In sulphuric acid-alcohol mixtures, thorium and uranium adsorption is independent of the DC of the alcohols employed, but thorium adsorption in nitric acid-alcohol media decreases with decreasing DC. This effect of DC on adsorption was earlier observed by Sakaki and Kakihana[109] in equilibrium experiments with K, Na, and Li ions in ethanol-water and methanol-water solutions, using a strongly acidic cation exchanger. (See also Section 5.)

III. *Effect of Mineral Acid Concentration on the Adsorption of Uranium and Thorium*

In order to investigate the effect of acidity on uranium and thorium adsorption, the over-all acidity of solutions of identical alcohol concentrations was varied, and the values for the distribution coefficients found are recorded in Figs. 6a, 6b and 6c. The theoretical interpretation of the shapes of the various curves obtained will be given in Section 5.

Discussion

Fig. 6a: The results in hydrochloric acid-alcohol mixtures show that the distribution coefficient of uranium at a given alcohol concentration increases practically linearly with the over-all acidity of the solution. Curve X, showing the results obtained by Fritz and Pietrzyk[70] in 74% isopropanol and 26% hydrochloric acid-mixture, deviates somewhat from this linearity. As can be seen from Fig. 1a, the distribution coefficient rises also at constant acidity with increasing alcohol content of the solutions. In pure aqueous hydrochloric acid solutions, the uranium adsorption is very low, but increases greatly, as earlier observed by Kraus and collaborators,[1–5] at higher hydrochloric acid concentrations. Distribution coefficients measured by Bunney *et al.*[6] under identical conditions, using the exchanger Dowex 2, $\times 8$, are somewhat lower at low acidities, but reach, at an over-all normality of 2·4*N* hydrochloric acid, values which are practically identical with those found by Kraus and collaborators.[1–5] It is therefore possible to adsorb uranium at relatively small over-all acidities from hydrochloric acid-alcohol media on strongly basic anion-exchange resins. Based on this fact, two methods for the adsorption and separation of uranium have been developed, by means of which uranium can be isolated and separated in 80% ethanol or 80% methanol-hydrochloric acid mixtures of 0·8*N* or 1·2*N* over-all acidity. It can further be seen from this figure (curve XII) that the distribution coefficient for thorium in 96% isopropanol + 4% hydrochloric acid shows no variation with the over-all acidity. At very low acid concentrations, the K_d decreases rapidly because of the hydrolysis of thorium tetrachloride. An effect resulting from acidity was also found by Fritz and Pietrzyk[70] in mixtures of 74% isopropanol + 26% hydrochloric acid and 65% isopropanol + 35% hydrochloric acid (see curves IV and IX). The K_d values found for thorium by these authors at such alcohol concentrations are in agreement with the values found by Korkisch and Tera[96] (see Fig. 1b). A considerable divergence exists between results for the K_d values of thorium found by Fritz and Pietrzyk[70] in ethanol-hydrochloric acid and the values found by Korkisch and Tera[96] in these media. Korkisch d Tera[96] oanbtained, for instance, in 96% ethanol, a distribution coefficient

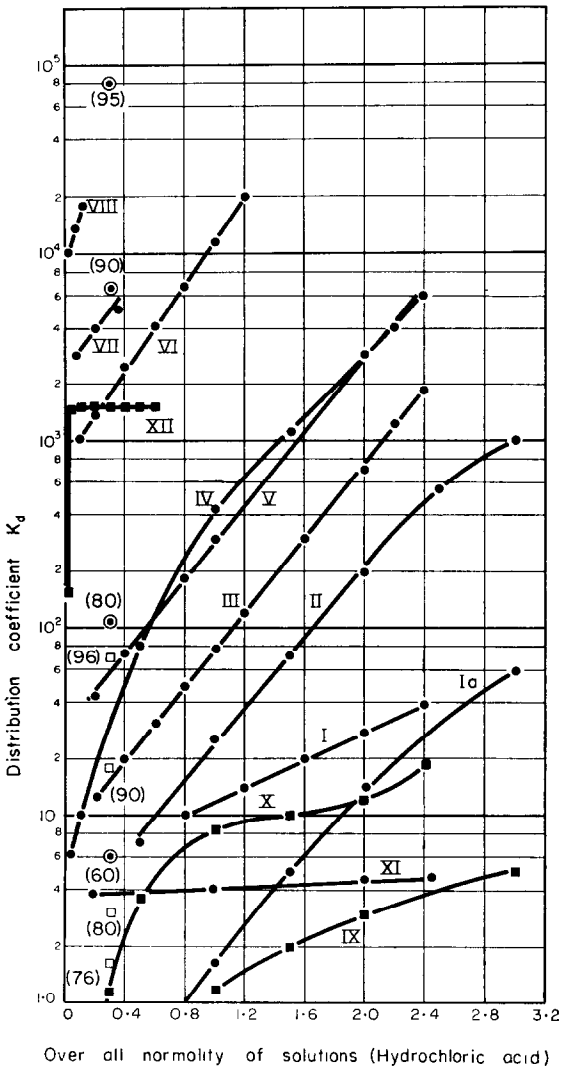


FIG. 6a.—Effect of hydrochloric acid concentration on the adsorption of uranium and thorium

I—Uranium; 100% HCl (Kraus and Nelson)[2]: Ia—Uranium; 100% HCl (Bunney *et al.*)[6]: II—Uranium; 55% isopropanol, 45% HCl (Fritz and Pietrzyk)[70]: III—Uranium; 60% ethanol, 40% HCl; IV—Uranium; 74% isopropanol, 26% HCl (Fritz and Pietrzyk)[70]: V—Uranium, 80% ethanol, 20% HCl: VI—Uranium; 90% methanol, 10% HCl: VII—Uranium; 94% methanol, 6% HCl: VIII—Uranium; 99% methanol 1% HCl: IX—Thorium; 65% isopropanol, 35% HCl (Fritz and Pietrzyk)[70]; X—Thorium; 74% isopropanol, 26% HCl (Fritz and Pietrzyk)[70]: XI—Thorium; 80% ethanol, 20% HCl: XII—Thorium; 96% isopropanol, 4% HCl (Amberlite IRA 400): ×—Thorium; 55% isopropanol, 45% HCl (Fritz and Pietrzyk)[70]: ○—Uranium in ethanol (% Ethanol) (Fritz and Pietrzyk)[70]; □—Thorium in ethanol (% ethanol) (Fritz and Pietrzyk)[70]

for thorium of 700 (compare with Fig. 1b), while the value found by Fritz and Pietrzyk[70] is only 70. This divergence may be explained by the high amounts of thorium used by the latter authors for their batch experiments. From Fig. 7b it may also be seen that there is a very pronounced effect of thorium concentration on the distribution coefficient of thorium when the amount of thorium adsorbed on the resin exceeds 10 mg/g of resin.

As the distribution coefficients of thorium and uranium at high alcohol concentrations reach very high values, simultaneous adsorption of both elements is possible, if longer-chain alcohols like propanol and butanol are employed, but not if methanol is used (see Fig. 1b).

It is noteworthy that thorium is adsorbed at all, since all investigations hitherto carried out in pure aqueous hydrochloric acid solutions have shown that thorium, because of its low tendency to form negatively charged chloride complexes, is not adsorbed on anion-exchange resins of the quaternary amine type, even from concentrated hydrochloric acid.[1,2] Quadrivalent uranium, however, is relatively well adsorbed from hydrochloric acid of higher normality on such resins.[1,2] This is astonishing, because thorium, as a rule, shows a very similar behaviour to quadrivalent uranium, and is known also, like uranium^{IV}, to form a comparable first chloride complex $ThCl^{3+}$ of similar stability.[110]

Fig. 6b: In nitric acid-alcohol solutions the adsorption of uranium is much less than in hydrochloric acid mixtures (in aqueous nitric acid solutions the conditions are till more unfavourable, as has been shown by Carswell[14] (see curve VII).

The distribution coefficients of uranium only reach values high enough for analytical purposes in solutions of high percentages of the longer-chained alcohols. This fact can be used for the simultaneous adsorption of uranium and thorium (see Section 4, Table III). Thorium, however, is much more strongly adsorbed from nitric acid solutions containing high percentages of methanol or ethanol than from hydrochloric acid-alcohol solutions (compare with Fig. 6a). Ready separation from uranium and other elements is therefore possible (see Section 4, Table II). In solutions of corresponding composition, the distribution coefficients of uranium are a linear function of the over-all normality (see curves IV, V and VI). At a lower alcohol concentration the uranium and thorium adsorption shows a linear increase, with increasing over-all normality slowly reaching a saturation value for uranium; and maxima for thorium which are followed by a decrease of the distribution coefficients with rising acidity. No maximum is reached for thorium, however, in 40% ethanol or in 40% methanol. As can further be seen from this figure no effect of the over-all acidity of the solution on the distribution coefficient of thorium was found only in solutions of very high methanol content. (A theoretical explanation for this phenomenon will be given in Section 5.)

From 0·6*N* to 0·005*N* (over-all normality) no hydrolysis of thorium nitrate occurred. Only when an over-all normality of 0·0025*N* nitric acid was reached could partial hydrolysis of thorium nitrate be observed; this is another proof of the considerably higher stability of the negatively charged thorium complex in comparison with the corresponding chloride complex—thorium chloride is already hydrolysed when a hydrochloric acid normality of 0·04*N* is reached.

Fig. 6c: It is seen that the highest distribution coefficients for uranium are reached in these sulphuric acid-alcohol media. As the distribution coefficient of uranium is

independent of DC and chain-length of the alcohols used (see also Figs. 4 and 5), curve IV was obtained by measuring the adsorption in 90% methanol + 10% sulphuric acid only. As comparison with curve III shows, the distribution coefficients in 80% and 90% alcohol differ only at over-all normalities of less than 0·2*N*. Comparing curves III and IV with the curves obtained by Kraus and Nelson[2] (curve I) and Bunney *et al.*[6] (curve Ia) for the effect of acidity in pure aqueous solutions, it is seen that at equal over-all normalities the distribution coefficients of uranium in alcohol solutions exceed the corresponding values obtained in pure aqueous-sulphuric acid solutions by about three orders of magnitude. The same can be said for thorium, as is shown in curves IIa (Bunney *et al.*[6]) and II (Janauer and Korkisch[98]) in comparison with curve VI. The

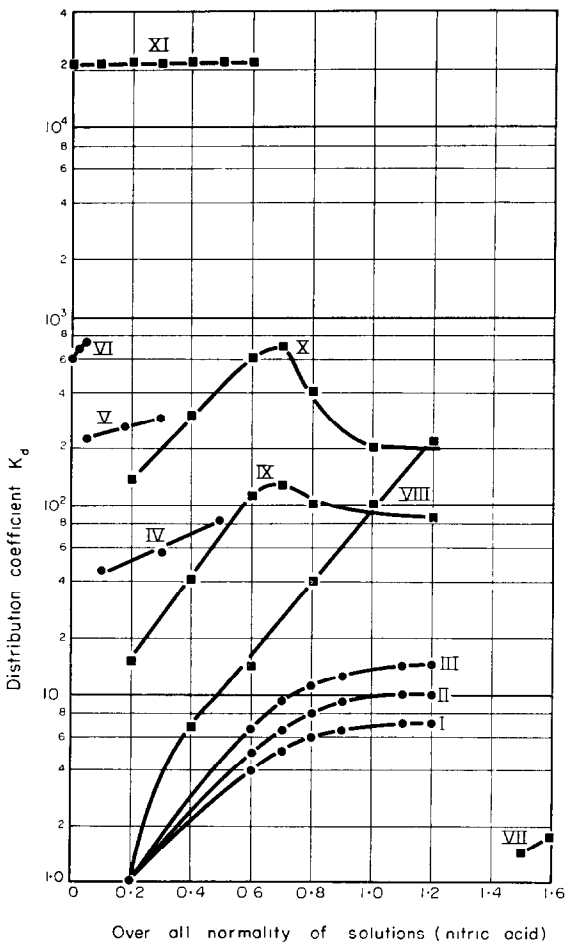


FIG. 6b.—Effect of nitric acid concentration on the adsorption of uranium and thorium I—Uranium; 40% ethanol, 60% HNO_3 (Korkisch *et al.*)[92]: II—Uranium; 60% ethanol, 40% HNO_3 (Korkisch *et al.*)[92]: III—Uranium; 80% ethanol, 20% HNO_3 (Korkisch *et al.*)[92]: IV—Uranium; 90% propanol, 10% HNO_3 (Korkisch and Tera)[103]: V—Uranium; 96% propanol, 4% HNO_3 (Korkisch and Tera)[103]: VI—Uranium; 99% propanol, 1% HNO_3 (Korkisch and Tera)[103]: VII—Thorium; 100% HNO_3 (Carswell)[14]: VIII—Thorium; 40% ethanol, 60% HNO_3 (Antal *et al.*)[95]: IX—Thorium; 60% ethanol, 40% HNO_3 (Antal *et al.*)[95]: X—Thorium; 80% ethanol, 20% HNO_3 (Antal *et al.*)[95]: XI—Thorium; 90% methanol, 4% HNO_3 (Tera *et al.*)[97].

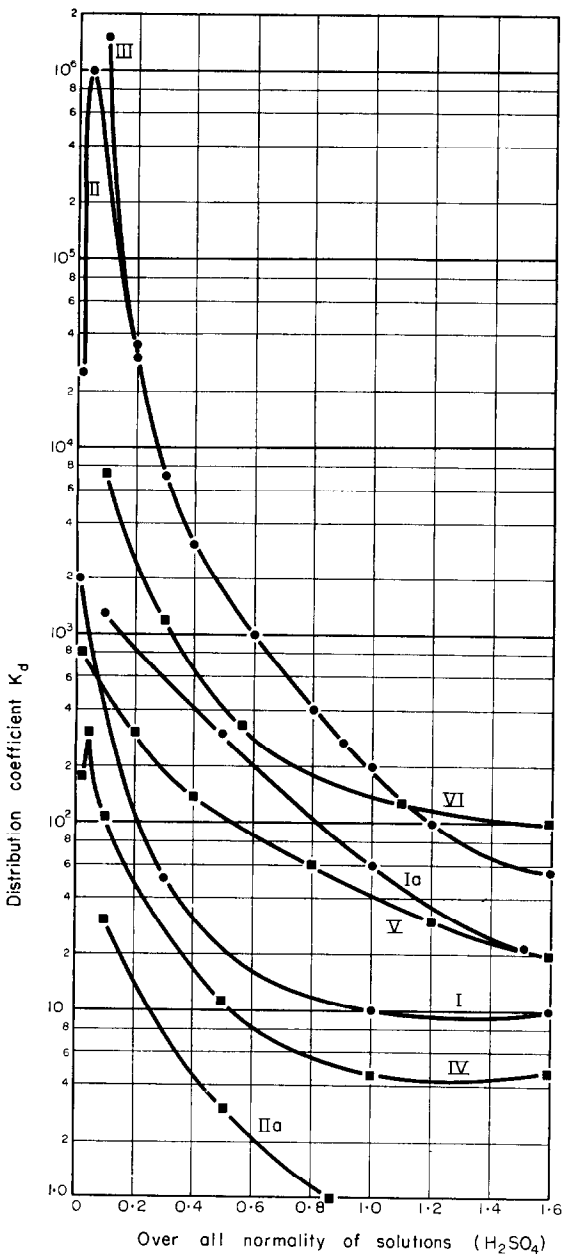


FIG. 6c.—Effect of sulphuric acid concentration on the adsorption of uranium and thorium

I—Uranium; 100% H_2SO_4, Dowex—1 (Kraus and Nelson)[2]: II—Thorium; 100% H_2SO_4 (Janauer and Korkisch)[98]: III—Uranium; 80% ethanol, 20% H_2SO_4 (Korkisch *et al.*)[92]: IV—Uranium; 90% methanol, 10% H_2SO_4 (Janauer and Korkisch)[98]: V—Thorium; 80% ethanol, 20% H_2SO_4 (Antal *et al.*)[95]: VI—Thorium; 90% methanol, 10% H_2SO_4 (Janauer and Korkisch)[98]: Ia—Uranium; 100% H_2SO_4, Dowex 2 (Bunney *et al.*)[6]: IIa—Thorium; 100% H_2SO_4, Dowex 2 (Bunney *et al.*).[6]

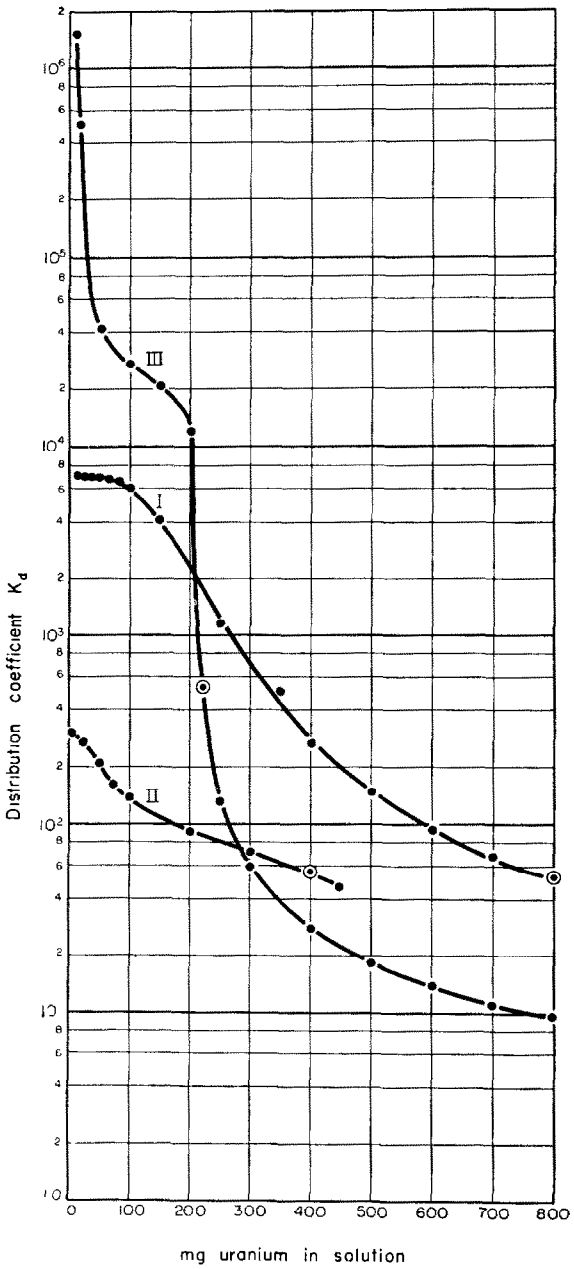


FIG. 7a.—Effect of concentration on the distribution coefficient of uranium I—Uranium; 90% ethanol, 10% 6*N* HCl (50 ml solution): II—Uranium; 96% n-propanol, 4% 5*N* HNO_3 (50 ml solution): III—Uranium; 90% n-propanol 10% 1*N* H_2SO_4 (25 ml solution): ○ Kd-values used for calculating the exchange capacities.

sudden decrease of the distribution coefficients of uranium and thorium below an over-all normality of 0·05*N* sulphuric acid (see curves II and III) is caused by the formation of neutral complexes of a higher order, which is equivalent to hydrolysis.

In conclusion, it can be said that on the basis of these results the simultaneous adsorption of uranium and thorium is feasible; it is, however, only applicable to technical processes[111] and is not to be recommended for analytical operations.

IV. *Effect of Concentration on the Distribution Coefficients of Uranium and Thorium Determination of Exchange Capacities*

The results of these investigations are shown in Figs. 7a and 7b.

Discussion

Fig. 7a: As may be seen from curve I, the distribution coefficient for uranium in 90% ethanol + 10% 6*N* hydrochloric acid shows no variations up to a concentration of

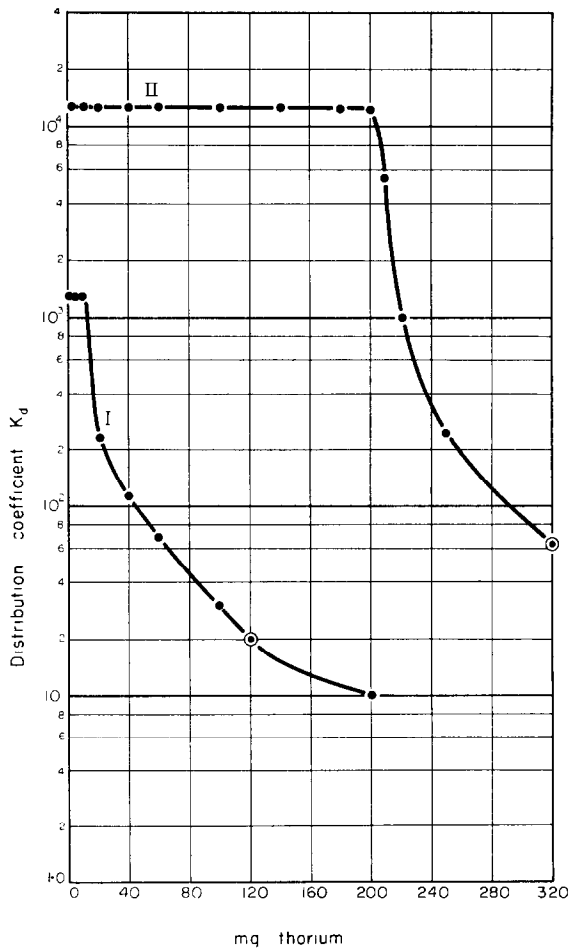


FIG. 7b.—Effect of concentration on the distribution coefficient of thorium
I—Thorium; 96% isopropanol, 4% 12*N* HCl (25 ml solution) Amberlite IRA 400):
II—Thorium; 90% methanol, 10% 5*N* HNO_3 (25 ml solution): ○ Kd-values used for calculating the exchange capacities.

50 mg of uranium. A steep descent is, however, observed at higher uranium concentrations, reaching a value of 35 when 1,000 mg of uranium are present in the solution. (The maximum exchange capacity of 412·5 mg of uranium/g of dry resin is reached when 800 mg or more of uranium are present in solution.)

From curve II for uranium in nitric acid, it is evident that the distribution coefficient remains constant only within a small range of concentrations. At a uranium concentration of 400 mg, the maximum capacity of the resin (212·5 mg of uranium/g of dry resin) is reached. In sulphuric acid-alcohol media a two-step curve was obtained (curve III), indicating the possible presence of two different uranyl sulphate complexes (see Section 5). The maximum capacity is reached in practice when 220 mg of uranium are present in solution. A value of 210 mg of uranium/g of dry resin was obtained.

Fig. 7b: The distribution coefficients of thorium in hydrochloric acid and nitric acid-alcohol solutions are shown as a function of the concentration of the solution. As may be seen from curve I (96% isopropanol + 4% 12*N* hydrochloric acid) the distribution coefficient for thorium remains constant up to 10 mg of the element, and falls off rather rapidly at higher concentrations. The capacity of the resin was found to be 58 mg of thorium/g of dry resin.

In nitric acid solutions the distribution coefficient does not vary over a fairly wide concentration range (curve II). However, when the thorium concentration exceeds 200 mg the K_d decreases rapidly at first and then somewhat more slowly. The exchange capacity of the resin was found to be 230 mg/g of dry resin for concentrations exceeding 320 mg of thorium/25 ml of solution.

As thorium sulphate is only sparingly soluble in sulphuric acid-alcohol solutions of high alcohol content ($2{\cdot}3 \times 10^{-5}$ moles of thorium are soluble in 1 liter of a mixture containing 90% methanol + 10% 2*N* sulphuric acid) no K_d-concentration plot was set up. The encircled points on the curves in Figs. 7a and 7b represent the uranium (thorium) concentrations where the maximum exchange capacities are reached. These points are thus equivalent to the beginning of the horizontal part of the adsorption isotherms corresponding to the K_d-concentration curves shown.

5. ION EXCHANGE SEPARATIONS IN MIXED SOLVENTS

Based on the experimental results given in Section 3 it was possible to develop seven isolation and separation methods for uranium and/or thorium in mixed alcohol-mineral acid solutions. The procedures briefly presented in the following three tables have already been described in detail elsewhere.[64,96,99–103]

Discussion

All the methods shown in Tables II–IV have in common the fact that separations of other elements from uranium or thorium in the corresponding media are the more difficult the higher the distribution coefficients of uranium and thorium under these conditions, since the adsorbability of the other elements increases too. On the other hand, high distribution coefficients allow the adsorption of large amounts of uranium or thorium. For micro-analytical purposes Methods (1) and (4) are suitable, where the distribution coefficients of uranium and thorium are not too high, but are nevertheless adequate.

As has been stated [Method (1)], a separation of uranium from tervalent iron is only possible if the sorption solution contains a reducing agent to transform tervalent iron

TABLE II.—METHODS FOR THE SEPARATION OF URANIUM AND THORIUM IN HYDROCHLORIC ACID-ALCOHOL MEDIA

Method	Composition of sorption solution	Anion-exchange resin	Elements separated from U and/or Th	Remarks
(1) Separation of uranium from thorium and other elements in hydrochloric acid-ethanol solution[100]	80% ethanol, 20% 4*N* HCl + ascorbic acid K_d for U = 200	Dowex-1 (Cl^- form)	Alkali metals, alkali earth metals, Mn^{II}, Al, Fe^{II}, Th, V^V, Zn, Sn, Cu, Co, Ni, Cr, Ti, Zr, rare earth elements, fluoride, sulphate, nitrate, phosphate, *etc.*[100]	Adsorbed on the resin are U, W, Mo, Bi and Pb. During the elution with 0·1*N* HCl saturated with diethyl ether, only U is eluted. To prevent the adsorption of Fe^{III} ascorbic acid has to be added to the sorption solution. This ion-exchange method can be employed for the assay of microgram amounts of U in practically all naturally occurring materials, as for instance silicate rocks, marine sediments[112,113] *etc.*
(2) Separation of U from Th and other elements in hydrochloric acid-methanol solution[101]	80% methanol, 20% 6*N* HCl + ascorbic acid K_d for U = 867	Dowex 1 (Cl^- form)	As above under (1)	U, Bi and Pb are adsorbed on the resin in the presence of ascorbic acid, or if present in higher amounts than 1 mg/100 ml each, Co, Ni and Cu are also adsorbed. The elution of U is performed with 1*N* HCl. This method can be used for the separation of microgram or milligram amounts of U from microgram or milligram amounts of other elements.
(3) Adsorption of Th from hydrochloric acid-isopropanol solution[96]	96% isopropanol, 4% 12*N* hydrochloric acid K_d for Th = 1,400	Dowex 1 or Amberlite IRA-400 (Cl^- form)	Alkali metals, alkali earth metals and some other elements not forming negatively charged chloride complexes.	This method can be used for the adsorption of microgram and milligram amounts of Th and in a modified form [see Table IV, method (6)] for the simultaneous adsorption of Th and U, with successive separation of these two elements.

TABLE III.—METHODS FOR THE SEPARATION OF Th IN NITRIC ACID-ALCOHOL MEDIA

Method	Composition of sorption solution	Anion-exchange resin	Elements separated from Th	Remarks
(4) Adsorption of Th from nitric acid-ethanol solution[99]	80% ethanol, 20% 3·5*N* nitric acid K_d for Th = 700 K_d for U = 9	Dowex 1 (nitrate form)	U, Ti, Zr, Fe, Al alkali-metals, nitrate, *etc.*[99]	Only Th is adsorbed on the resin. The elution of Th is performed with 0·1*N* nitric acid saturated with diethyl ether. Interference only in presence of high amounts of fluoride or phosphate. This method enables the determination of micrograms of Th in silicate rocks, marine sediments and other materials.[99,112,113]
(5) Separation of Th from U and other elements in nitric-acid-methanol solution[64]	90% methanol, 10% 5*N* nitric acid K_d for Th = 12,475 K_d for U = 33	Dowex 1 (nitrate form)	Fe^{III}, Co, Ni, Cu, Ag, Mg, Ca, Sn, Zn, Cd, Al, Y, Ti, Zr, Hf, V^{V}, Cr^{III}, Mo^{VI}, Mn^{II}, UO_2^{2+}, alkali metals, phosphate, chloride, sulphate and nitrate	Th, Ba, Pb, Bi, La Ce and other rare earth elements are adsorbed on the resin. The elution is performed with 1*N* nitric acid. Interference only caused by the co-adsorbed elements, if they are present in amounts exceeding 10 mg each. This procedure can be used for the quantitative separation of microgram and milligram amounts of Th. Pu^{IV} should under these conditions show a rather similar behaviour to Th[115,116]

to the bivalent form [see Methods (1) and (2)]. Among the reducing agents investigated, ascorbic acid turned out to be the most suitable, as it causes no interference in the column operations. Moreover, reduction of $uranium^{VI}$ to $uranium^{IV}$ does not take place under the conditions employed. The reducing effect of ascorbic acid on tervalent iron increases with decreasing concentrations of hydrochloric acid and alcohol (because of increasing complex formation of the tervalent iron ion with increasing hydrochloric acid and alcohol concentration). Because of this, the reduction of iron in Method (1) is more complete than it is in Method (2), where higher amounts of ascorbic acid must be used. A separation of thorium and iron cannot be affected in hydrochloric acid mixtures, since the necessary high alcohol concentrations inhibit the

TABLE IV. METHODS FOR THE SIMULTANEOUS ISOLATION AND SUBSEQUENT SEPARATION OF URANIUM AND THORIUM

Method	Composition of sorption solution	Eluants	Anion-exchange resin	Elements separated	Remarks
(6) Adsorption of U, Th, and Bi from nitric acid-propanol solution and separation of U, Th and Bi[102]	96% n-propanol, 4% 5*N* nitric acid K_d for U = 300 K_d for Th = 5,000 K_d for Bi = 4,000	For U: 80% methanol, 20% 5*N* nitric acid For Th: 80% methanol, 20% 6*N* hydrochloric acid For Bi: 1*N* nitric acid	Dowex 1 (nitrate form)	U, Th, Bi	This method is applicable for the separation of microgram and milligram amounts of U, Th and Bi. The determination of Bi was carried out using the well known bismuth iodide method.[114]
(7) Adsorption of Th and U from hydrochloric acid-butanol solution and separation of these elements from each other in hydrochloric acid-methanol solution[103]	90% n-butanol, 10% 6*N* hydrochloric acid K_d for Th = 250 K_d for U = 2,600	For Th: 90% methanol, 10% 6*N* hydrochloric acid For U: 1*N* hydrochloric acid.	Dowex 1 (nitrate form)	U, Th	This technique can be employed for the separation of microgram amounts of U and Th.

reduction of iron by ascorbic acid. In nitric acid solutions the separation of iron from thorium is very effective. Separation of uranium from thorium can be performed with practically all the above cited methods.

For simultaneous adsorption of uranium and thorium, Methods (6) and (7) can be employed successfully, utilising mixtures of very high alcohol content of higher aliphatic alcohols (90–96%) because otherwise the distribution coefficients for uranium would not be sufficiently high.

The precision of the individual methods described above for the various separations is, because of the completely quantitative adsorption or separation of uranium and/or thorium in practice, given by the precision of the polarographic, spectrophotometric or fluorimetric methods used for the final determination of these radioelements.

5. GENERAL THEORETICAL ASPECTS OF ION EXCHANGE IN MIXED SOLVENTS AND DISCUSSION OF RESULTS

Ion exchange in mixed and non-aqueous solutions is far less understood than ion exchange in pure aqueous systems; theoretical treatment is difficult because of the lack of sufficient data on the behaviour of electrolytes in mixed media. It is, however, a well known fact that the replacement of part of the aqueous phase by an organic solvent often enhances the ion-exchange absorbabilities of inorganic ions. In addition, the equilibrium quotient or selectivity coefficient for a given pair of ions is often higher when these ions are dissolved in a mixed or non-aqueous solvent, than when they are dissolved in water.[89,117,118]

The replacement of water by a non-aqueous solvent in an ion-exchange system can be expected to influence,[104] both in the solution and in the resin phase:

(*a*) Solvent uptake and swelling of the resin

(*b*) Dissociation
(*c*) Solvation
(*d*) Complex formation
(*e*) Ionic and molecular interaction.

These factors must be regarded as a coherent complex of mutually related variables.

Solvent uptake and swelling is primarily caused by the solvation tendency of all ions inside the resin phase, together with the electrostatic repulsion between the exchange sites of the matrix; or generally speaking, by osmotic and electrostatic forces acting against the tension of the resin matrix. Experiments have in many cases shown a relationship between solvent uptake and polarity of the solvent; the more polar the solvent the greater, usually, is the amount of solvent taken up, and hence the greater is the swelling of the resin, while solvents of low polarity are as a rule taken up to a less extent and produce less swelling.[72,117,119–124] For a mixture of water with an organic solvent, *e.g.*, acetone, in contact with an ion-exchange resin, it follows that water will be concentrated in the resinous phase[72,88,125] while the solution will be richer in the organic solvent. Thus the distribution of an ion between its solution and the ion-exchange resin in a mixed system cannot be regarded merely as an ion-exchange equilibrium but at the same time also as a partition between two liquid phases of different composition. The "selective solvent uptake" by a resin becomes more accentuated with decreasing water content of the mixed solvent and increasing cross linkage of the polystyrene matrix.[122,126,127]

That the ion-exchange resins swell less in solvents of smaller dielectric constant (DC) can be readily explained by Bjerrum's theory[128] of ion-pair formation. As ionic interaction increases with decreasing DC of the solvent, dissociation is repressed, and ion-pairs or even -triplets[129] can be formed, with the result that the effective number of osmotic-active exchange ions will diminish. Less swelling of a resin, like increased cross-linkage, causes an increase of selectivity coefficients.[117] Resin swelling is, however, not only influenced by the effect of polarity of the solvent on the ionic interaction, but also by the loading[122,123,126,127] of the resin, and by polar interactions as well as by dispersion interactions[130] between the solvent molecules and the resin. Solvent-uptake and swelling increase with increased similarity between the structure of the solvent molecules and the functional and structural groups of the matrix. The swelling of strong-base anion exchangers of the quaternary amine type in alcohols may be taken as a typical example of these effects, since the functional groups of these exchangers show a very high affinity for alcohols; this can compensate the contrary influence of the (compared with water) lower polarity of these solvents. Some authors[119,120] claim that resins of this type swell even more in methanol or ethanol than in water, while others[122,123] find that water, in comparison with alcohols, is still preferentially sorbed by such resins (but to a much less extent than by cation exchangers of the sulphonic acid type.)

Solvation and complex formation play a most important role in ion-exchange equilibria in mixed solvents. The substitution of increasing amounts of water by an organic solvent leads to stepwise dehydration[80] of the hydrated ions, to a progressive increase of ionic interaction, and hence to association in the mixed solution. It has been shown that the stability of negatively charged complexes,[1–21,131] *e.g.*, chlorocomplexes of cations in solution, can be markedly enhanced by the introduction of organic solvents.[70,80,81,92–98] This makes possible the adsorption of cationic elements which are

only weakly, or almost not at all, adsorbed from pure aqueous solution as anionic complexes on anion-exchange resins. On the other hand, organic solvents can also serve to bring about selective elution, by complex formation with the ion to be removed from the resin.[76,88] In such a way selectivity coefficients can be greatly increased. The high adsorbabilities which are sometimes encountered in mixed-solvent ion-exchange systems can be explained by neutral adsorption.[71,87,119] Dissociation of the electrolyte is repressed by the low-DC solvent and the hydrophilic electrolyte is "extracted" as the "entire salt"[87] into the resin phase, where water is concentrated as mentioned above. On the other hand neutral adsorption will also be promoted by the uptake of solvents of low DC into the resin.

High concentration and low DC will both intensify ionic interaction and pair formation. The ionic activities in the resin are correspondingly diminished, and consequently the interface potential (Donnan-potential) will be considerably reduced.[104] A decrease of the interface potential means that strong electrolytes, which are otherwise kept out (ion-exclusion), can enter the resin.

Several other factors, such as, for instance, the influence of ionic radii (solvated and unsolvated), ionic charge, ionic strength, the pH of the solution, which influence ion-exchange equilibria in mixed solvents, have not been discussed in the crude qualitative treatment given above; these must be taken into account if a particular system is to be investigated quantitatively. Severe limitations are, however, imposed in many cases by the lack of sufficient data on the behaviour of electrolytes in such systems.

Despite this complexity, an attempt has been made to approach the problem simply from the viewpoint of the DC of the solvent,[93,109,122,123,132] which seems to be justified to some extent because of the effect of the polarity of the solvent on resin swelling and on dissociation and complex formation, as already discussed. On the other hand, there are exceptions[117–120] to the parallelism between resin swelling and the DC of the solvent (caused for instance by interactions between resin and solvent molecules), and it is as yet impossible to calculate the DC within the resin phase.[104] Although apparently general quantitative information cannot be derived from the macroscopic DC of a solvent, it still seems possible to make qualitative predictions in some cases. Experiments with cation exchangers[89,132] have shown that in mixtures of some solvents of low DC with water the selectivity coefficients increase with increasing content of organic solvent; this can be taken as the effect of decreasing the DC of the solutions. Selectivity coefficients of various exchangers have been observed to increase in solvent mixtures where the organic solvent was replaced by a solvent with a similar type of molecular structure, but having a lower DC.[109,117,118] In our experiments (Section 3, Part II, 1 and 2) we have found that the effect of DC and chain length on the adsorption of uranium^{VI} and thorium^{IV} from ROH-mineral acid systems on strong-base anion exchangers is, in three cases out of six (uranium in HCl- and HNO_3-ROH and thorium in HCl-ROH), the expected effect (rise of K_d with decreasing DC); while in two cases no effect of DC was observed (uranium and thorium in H_2SO_4-ROH) and in one case there was actually a reverse effect, *i.e.*, a decrease of K_d with growing DC and chain length of the alcohols was found (thorium in HNO_3-ROH, see Fig. 5). For this last no theoretical explanation can be offered. Yet in all mixtures of a given alcohol, the adsorption increased with increasing percentage of the alcohol (and decreasing DC) in the solution; and in any mixture containing any alcohol the adsorption was higher than if this alcohol was replaced by water. It may be mentioned here

that a study of the adsorption behaviour of vanadium^{IV} and vanadium^{V} in hydrochloric acid-alcohol solutions, which was earlier described,[81] showed almost the same relationship between alcohol chain length (and also DC) and K_d as uranium^{VI} and thorium^{IV} under corresponding conditions. So far it seems that where the effect of the DC of the solvent on the adsorption of ions from acid-solvent mixtures on strong-base anion exchangers is concerned, with a few exceptions only systems containing the same mineral acid in the same concentration, and solvents of a very similar molecular structure (homologous alcohols, ketones, ethers, *etc.*), can be compared.

Thermodynamically there are three mechanisms of adsorption possible[133] for anion exchange on strong-base anion exchangers:

Mechanism I: Strong anionic complexes are formed in solution, and these are regularly exchanged with the counter-ions of the exchanger.

1. *Complex formation:*

$$A^{n+} + bB^{m-} \rightleftharpoons (AB_b)^{(m-n)-}$$

2. *Anion exchange:*

$$(AB_b)^{(m-n)-} + \overline{(m-n)\cdot[(R_s^+)(C^-)]} \rightleftharpoons \overline{[(R_s^+)_{(m-n)}(AB_b)]^{(m-n)-}} + (m-n)C^-$$

Mechanism II: Because of insufficient stability of the charged complex in the liquid phase, the formation of the neutral complex is favoured; this diffuses into the resin, where it is bound by the counter-ions as a complex with several ligands.[71,134,135]

1. *Complex formation:*

$$mA^{n+} + nB^{m-} \rightleftharpoons A_mB_n$$

2. *Adsorption:*

$$A_mB_n + \overline{x[(R_s^+)(C^-)]} \rightleftharpoons \overline{[(R_s^+)_x(A_mB_n)(C^-)_x]}$$

Mechanism III. The cations which exist in solution can only enter the resin if the counter-ions have at least one exchangeable proton:

1. *Proton exchange:*

$$n(CH)^{m-} + A^{n+} \rightleftharpoons (C_nA)^{m-} + nH^+$$

2. *Anion exchange:*

$$(C_nA)^{m-} + \overline{[(R_s^+)m(CH)^{m-}]} \rightleftharpoons \overline{[(R_s^+)_m(C_nA)^{m-}]} + (CH)^{m-}$$

A^{n+} = cation of charge n+
B^{m-} = anion of charge m−
b = number of anions to form the anionic complex $(AB_b)^{(m-n)-}$ in solution with a negative charge of (m − n)−
R_s^+ = bound cation (resin phase)
C = counter-ion
x = number of ligands
$(CH)^{m-}$ = complex anion of charge m−, containing an exchangeable H [*e.g.*, $(SO_3H)^-$)]. Components covered by a bar are in the resin phase.

The existence of negatively charged uranyl and thorium complexes[1–21,133–137] has earlier been established (except for thorium in hydrochloric acid medium.) It is believed, however, that at higher alcohol concentrations, especially with the higher alcohols, ion-exchange adsorption has neutral adsorption increasingly superimposed on it, as has been postulated by Katzin and Sullivan[87] for the adsorption of uranyl chloride and uranyl nitrate from oxygen-containing organic solvents on strong-base anion-exchange resins, and by Tera and Korkisch for their adsorption from hydrochloric acid-[93] and nitric acid[94]-alcohol systems on such resins.

To establish the formulae of the complexes in the systems where highest adsorption occurred, the exchange capacities of Dowex 1 for uranium and thorium (see Section 3, part IV) have been determined by constructing the corresponding adsorption isotherms. In this paper the variation of the distribution coefficient with increasing concentration (see Figs. 7a and 7b) is emphasised, in order to make the analytical applicabilities more obvious. The encircled points in these figures (pp. 971–2) are equivalent to the beginning of the horizontal part of the corresponding adsorption isotherms, where the resin is already saturated with the ion in question. The exchange capacity can be calculated there, or for other points on the curve, using the simple relationship:

$$\text{mg of uranium or thorium/g of resin} = \frac{K_d \times W}{V_s + K_d}$$

W = mg of uranium or thorium in solution before the addition of the resin
V_s = volume of the solution.

The maximal amount of uranium or thorium taken up by the resin (= exchange capacity = C_e) was used for calculating the number of negative charges of the complexes in the resin phase, by means of the formula:

$$n = \frac{3{\cdot}4 \times A}{C_e}$$

A = atomic weight of adsorbed element (uranium or thorium)
3.4 = capacity of the resin (chloride, nitrate or sulphate; see Section 2, part IV) in mg equiv./g of dry resin
n = number of negative charges in the complex
C_e = exchange capacity of the resin for uranium or thorium in mg/g of dry resin under the conditions selected.

The values found for n were as follows:

UO_2^{2+} in 90% ethanol + 10% 6*N* HCl	2
UO_2^{2+} in 96% n-propanol + 4% 5*N* HNO_3	4
UO_2^{2+} in 90% n-propanol + 10% 1*N* H_2SO_4	4
Th^{4+} in 90% isopropanol + 4% 12*N* HCl	13·6
Th^{4+} in 90% methanol + 10% 5*N* HNO_3	3·4

(Neither the adsorption isotherm nor a K_d-concentration plot were set up for thorium sulphate in H_2SO_4-alcohol medium because of its low solubility in this system.)

The negatively charged uranyl complexes calculated from the above values correspond to the formulae:

$$(UO_2(Cl)_4)^{2-} \quad (UO_2(NO_3)_6)^{4-} \text{ and } (UO_2(SO_4)_3)^{4-}.$$

For thorium in hydrochloric and nitric acid-alcohol media no stoicheiometric formulae could be derived.

To support the above postulates concerning the adsorption mechanism of uranyl and thorium (combination of mechanisms I and II) we shall discuss in detail the adsorption of uranyl chloride from hydrochloric acid alcohol mixture on Dowex 1, and then the other systems more briefly. Mechanism I is known to take place in aqueous hydrochloric acid solutions as shown by Kraus and collaborators[1–5] and can be written:

1. $UO_2Cl_2 + 2\ Cl^- \rightleftharpoons UO_2(Cl)_4)^{2-}$
2. $(UO_2(Cl)_4)^{2-} + \overline{2(R_s^+Cl^-)} \rightleftharpoons \overline{((R_s^+)_2(UO_2)(Cl_4^{2-})} + 2\ Cl^-$

From equation 1 it is evident that increasing concentration of chloride ions should favour complex formation and hence adsorption. Since the increase of hydrochloric acid concentration also strongly increases the adsorption of uranyl chloride from hydrochloric acid-alcohol mixtures (see Fig. 6a, Section 3), mechanism I appears to be valid in such systems. If it is considered that there is a direct addition of uranyl chloride to the resin, mechanism II can be represented:

$$UO_2Cl_2 + 2\,\overline{(R_s^+Cl^-)} \rightleftharpoons \overline{((R_s^+)_2(UO_2\,(Cl)_4^{2-})}$$

This mechanism is supported by the fact that equilibrium is attained almost immediately in hydrochloric acid-alcohol mixtures with a high percentage of alcohol; this can be observed visually by the rapid loss of colour of the solution after addition of the anion exchanger.[71] Measurements show that 5 min after the resin is brought into contact with the uranium-containing solution (90% ethanol + 10% 6*N* hydrochloric acid) more than 90% of the exchange capacity is reached.

Since the diffusion rate is a function of the radius of the solvated ion in question, and since a neutral complex will be much less solvated than a charged one, mechanism II seems also to apply here. Further, it was observed that UO_2Cl_2 was also considerably adsorbed from mixtures containing water and alcohols in the absence of hydrochloric acid,[93] supporting the assumption that mechanisms I and II occur simultaneously. The existence of only one negatively charged chloro complex of uranium is obvious from Fig. 6a, since the slope,

$$\mathrm{tg}\alpha = \frac{\text{charge of complex}}{\text{charge of complexing anion}} = \frac{\mathrm{d}\log K_d}{\text{d log normality of acid}},^{133}$$

of the K_d acidity curves shows practically no deviation from linearity. Since the adsorption of thorium from hydrochloric acid-alcohol mixtures of low alcohol content (see Fig. 6a, curves X, XI and XII) increases with increasing hydrochloric acid concentration, mechanism I seems to be partly responsible for the adsorption. At a very high alcohol concentration, however (see Fig. 6a, curve XIII), K_d does not vary with acidity; this can be taken as evidence for mechanism II, indicating that only neutral adsorption occurs under these conditions. Further evidence comes from the fact that no stoicheiometric amount of thorium is taken up by the resin (see above, page 980).

For the adsorption of uranium nitrate in nitric acid-alcohol mixtures, mechanism I seems to apply; this can be concluded from the increase of K_d with acidity (see Fig. 6b, curves I–VI), although it diminishes at acidities higher than 0·7*N*, so that the K_d reaches a saturation value. At high alcohol concentration mechanism II will prevail. From the linearity of curves IV–VI it follows that only one negatively charged uranium complex is present, the composition of which (for the formula see above was calculated for a 96% n-propanol-4% nitric acid mixture.

The adsorption of thorium nitrate from nitric acid-alcohol solutions shows an increase of neutral adsorption with increasing alcohol concentration (compare curves VIII–XI, Fig. 6b). Mechanism I accounts for the linear increase of the distribution coefficient with increasing acidity in 40% alcohol (curve VIII). The maxima in curves IX and X correspond to the maximal molality of the neutral complex in solution, as has been pointed out by Antal,[133] who proved that the increase of K_d with the acidity

at low nitric acid concentrations (left hand side of the maxima) is the result of mechanism I, whereas the increase of K_d with decreasing acidity at higher nitric acid concentration (right hand side of the maxima) is caused by mechanism II (increasing neutral adsorption). At very high alcohol percentage in the mixture (curve XI), no effect of acidity on the distribution coefficient was observed, suggesting that only neutral adsorption (mechanism II) takes place. Since even in 90% methanol + 10% 5*N* nitric acid mixture more than the theoretical amount of thorium nitrate is adsorbed on the resin, this can be taken as definite proof of the existence of neutral adsorption. Under these conditions, 3·96 mg equiv of thorium or 230 mg were taken up by the resin, which has a real capacity of only 3·4 mg equiv of thorium/g (see Section 2 and Fig. 7b, Section 3), so that no stoicheiometric formula for a thorium nitrate complex could be established.

Since mechanism II has already been confirmed for the adsorption of uranyl sulphate in pure aqueous sulphuric acid solution by Arden and Wood,[134] the introduction of alcohol should be expected to enhance neutral adsorption further. That this is really the case may be deduced from the fact that the distribution coefficients in such media are extremely high at high alcohol concentrations and very low acidity. (See Fig. 6c). The uranyl trisulphato complex corresponding to the formula derived from our results (see above, page 970) is in accordance with that obtained by Arden and Wood[134] in aqueous sulphuric acid. As the first "step" in curve III (Fig. 7a) seemed to imply the existence of a higher charged sulphato complex, n was calculated for the middle of the step (135 mg uranium originally in soln, $K_d \simeq 22{,}000$) and found to be $\sim$6. This is another proof of the existence of the complex $[(UO_2)(SO_4)_4]^{6-}$, which was also postulated by the above mentioned authors.[134] Neither of these highly charged negative complexes is, however, believed to exist in measurable amounts in solution. The investigations of Antal,[133] who has postulated the existence of several thorium sulphate complexes, including neutral complexes such as $[Th(SO_4)_2]^\circ$ and $(ThOSO_4)^\circ$, in the resin phase, as well as the results of our own experiments (see Fig. 6c), suggest that thorium is also adsorbed from sulphuric acid-alcohol mixtures in the same way as uranium (mechanism II).

In conclusion, it might be said that much more research will have to be conducted in the field of the anion exchange of uranium and thorium in mixed and non-aqueous solvents, before we will have gained complete understanding of the subject; but current investigations are likely to lead to the development of useful new analytical methods in the near future.

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Zusammenfassung—In der vorliegenden Arbeit werden die bis jetzt veroeffentlichten Resultate hinsichtlich des Anionaustauschverhaltens von Uranium (VI) und Thorium (IV) in Loesungsmittelgemischen zusammengefasst und das Adsorptionsverhalten dieser beiden Radioelemente am stark basischen Anionenaustauscher Dowex 1 in Mischungen bestehend aus Salz-, Salpeter-oder Schwefelsaeure und aliphatischen Alkoholen genau beschrieben. Die Verteilungskoeffizienten bei verschiedenen Saeurenormalitaeten, Alkoholkonzentrationen, Uran- und Thoriumkonzentrationen sowie bei den unterschiedlichen Kettenlaengen und Dielektrizitaetskonstanten der angewendeten Alkohole werden angegeben. Ausserdem werden einige auf Grund dieser Resultate entwickelten Trennungsverfahren des Urans bezw. Thoriums

voneinander oder von anderen Elementen beschrieben. Abschliessend werden theoretische Betrachtungen ueber die Art, wie diese beiden Elemente adsorbiert werden, angestellt.

Résumé—Cet article résume les résultats importants obtenus jusqu'à présent sur le comportement de l'uranium (VI) et du thorium (IV) sur résine échangeur d'anions dans des mélanges de solvants, ainsi que les résultats de travaux de recherches effectuées au laboratoire. Les auteurs se proposent de donner une description détaillée du comportement de ces actinides sur des résines échangeurs d'anions fortement basiques dans des solutions d'acide minéral contenant des alcools aliphatiques. Les études d'équilibre ont montré que les coefficients de partage varient beaucoup avec l'acide utilisé comme le montrent les résultats récents obtenus dans les systèmes aqueux. Dans les mélanges d'un acide minéral donné avec différents alcools, les coefficients de partage dépendent du pourcentage d'alcool, de l'acidité des solutions, des constantes diélectriques et des longueurs de chaîne des alcools utilisés. Les résultats de ces recherches peuvent être appliqués à la séparation du thorium et de l'uranium, d'une part l'un de l'autre, d'autre part pratiquement de tous les cations et les anions. Deux des méthodes de séparation mises au point ont déja été appliquées au dosage de l'uranium et du thorium dans des produits de composition très variée. Finalement les aspects théoretiques généraux de l'échange anionique dans des mélanges de solvants sont discutés et les résultats obtenus pour l'uranium et le thorium sont interprétés par conséquence.

REFERENCES

[1] K. A. Kraus and F. Nelson, Symposium on *Ion Exchange and Chromatography in Analytical Chemistry*. ASTM Special Technical Publication No. 195. American Society of Testing Materials. Philadelphia, 1958, pp. 27–57.
[2] *Idem, Proceedings, Intern. Conference on Peaceful Uses of Atomic Energy*, **7**, 113, 131. United Nations, 1956.
[3] K. A. Kraus, G. E. Moore and F. Nelson, *J. Amer. Chem. Soc.*, 1956, **78**, 2692.
[4] *Idem, ibid.*, 1955, **77**, 3972.
[5] K. A. Kraus and F. Nelson, *Ann. Rev. Nuclear Sci.*, 1957, **7**, 31.
[6] L. R. Bunney, N. E. Ballou, J. Pascual and S. Foti, *Analyt. Chem.*, 1959, **31**, 324.
[7] D. H. Wilkins and L. E. Hibbs, *Analyt. Chim. Acta*, 1959, **20**, 427.
[8] D. H. Wilkins, *ibid.*, 1959, **20**, 271.
[9] *Idem, ibid.*, 1959, **20**, 273.
[10] *Idem, ibid.*, 1958, **18**, 372.
[11] *Idem, ibid.*, 1957, **16**, 449.
[12] D. Jentzsch, *Z. analyt. Chem.*, 1956, **152**, 134.
[13] R. F. Buchanan and J. P. Faris, RICC/173, U.S.A, 1960.
[14] D. J. Carswell, *J. Inorg. Nuclear Chem.*, 1957, **3**, 384.
[15] J. Danon, *ibid.*, 1958, **5**, 237.
[16] *Idem., J. Amer. Chem. Soc.*, 1956, **78**, 5953.
[17] Ying-Mao Chen, Chia-Tsung Lin and Tung-Ho Chen, *J. Chinese Chem. Soc.* (*Taiwan*), Ser. II. 1955, **2**, 111; *Chem. Abstr.*, 1956, **49**, 15619g.
[18] L. I. Katzin, *The Actinide Elements*. Nat. Nucl. Energy Series, Div. IV, Vol. 14 A. McGraw-Hill, N.Y., 1954, Chap. 4., p. 70.
[19] I. C. Hindman, *ibid.*, Chap. 9, p. 341.
[20] J. L. Jenkins and R. J. Richardson, AERE C/R 1217, 1953.
[21] N. Saito and T. Sekine, *Bull. Chem. Soc. Japan*, 1957, **30**, 561.
[22] J. Korkisch, A. Farag and F. Hecht, *Z. analyt. Chem.*, 1958, **161**, 92.
[23] E. Tomić, I. M. Ladenbauer and M. Pollak, *ibid.*, 1958, **161**, 28.
[24] G. W. C. Milner and J. W. Edwards, *Analyt. Chim. Acta*, 1957, **17**, 259.
[25] F. Hecht, J. Korkisch, A. Thiard and E. Tomić, *Austrian pat.*, 206, 409, May 15, 1959.
[26] Yu. V. Morachevskij and M. N. Gordeeva, *Vestn. Leningr. Univ.*, 1959, **10** (part 2), 148.
[27] L. Wish and M. Rowell, U. S. Atomic Energy Comm., Rep. USNRDL-TR-117, 1956.
[28] H. M. Ockenden and J. K. Foreman, *Analyst*, 1957, **82**, 592.
[29] J. Korkisch, M. R. Zaky and F. Hecht, *Mikrochim. Acta*, 1957, 485.
[30] M. Novak and V. Pekarek, *Jaderna Energia*, 1958, **4**, 256.

[31] A. E. Bearse and R. A. Ewing, Battelle Memorial Institute Progress Report, December 1948, JDS-158.
[32] G. A. Welford and J. S. Alercio, NYO-4501.
[33] *Idem*, NYO-4694.
[34] A. Preuss, private communication.
[35] S. Fischer, U.S. Atomic Energy Comm., Document RMO-2530 1954.
[36] *Idem., ibid.*, Document RMO-2531 1954.
[37] S. Fisher and R. Kunin, *Intern. Conf. on the Peaceful Uses of Atomic Energy*, A/CONF. 8/P/818, USA, 1955.
[38] R. F. Hollis and McArthur, *ibid.*, A/CONF. 8/P/526, 1955.
[39] A. Arnfelt, *Acta Chem. Scand.*, 1955, **9**, 1484.
[40] H. J. Seim, R. J. Morris and D. W. Frew, U.S. Atomic Energy Comm., Rept. RMO-2680, 1956.
[41] *Idem, ibid.*, Document UN-TR-5, 1956.
[42] *Idem, Analyt. Chem.*, 1957, **29**, 443.
[43] S. Fisher and R. Kunin, *ibid.*, 1957, **29**, 400.
[44] A. D. Horton, P. F. Thomason and M. T. Kelley, *ibid.*, 1957, **29**, 388.
[45] G. A. Welford and D. Sutton, Report NYO-4755, Feb. 7, 1957.
[46] M. V. Šušić, *Bull. Inst. Nuclear Sci.*, "Boris Kidrich", Belgrade, 1957, **7**, 35.
[47] H. J. Seim and R. J. Morris, U.S. Atomic Energy Comm., Rept. RMO-2682, 1958.
[48] C. V. Banks, J. A. Thompson and J. W. O'Laughlin, *Analyt. Chem.*, 1958, **30**, 1792.
[49] G. Banerjee and A. H. A. Heyn, *ibid.*, 1958, **30**, 1795.
[50] M. L. Borlera, *Ricerca Sci.*, 1958, **28**, 331.
[51] H. J. Seim, R. J. Morris and R. G. Pastorino, *Analyt. Chem.*, 1959, **31**, 957.
[52] G. Jangg, W. Ochsenfeld and F. Habsahi, *Z. analyt. Chem.*, 1959, **171**, 27.
[53] F. Habashi, *Mikrochim. Acta*, 1959, 932.
[54] L. Wish, *Analyt. Chem.*, 1959, **31**, 326.
[55] Y. Marcus, *2nd United Nations Intern. Conf. on Peaceful Uses of Atomic Energy*, Session A-15, P/1605, Geneva, Switzerland, 1958.
[56] E. C. Freiling, J. Pascual and A. A. Delucchi, *Analyt. Chem.*, 1959, **31**, 330.
[57] L. Wish, *ibid.*, 1960, **32**, 920.
[58] T. K. S. Murthy, *Analyt. Chim. Acta*, 1957, **16**, 25.
[59] F. Hecht, J. Korkisch, R. Patzak and A. Thiard, *Mikrochim. Acta*, 1956, 1283.
[60] J. Korkisch, A. Thiard and F. Hecht, *ibid.*, 1956, 1422.
[61] J. Korkisch, Thesis, University of Vienna, 1957.
[62] J. Korkisch, A. Farag and F. Hecht, *Mikrochim. Acta*, 1958, 415.
[63] J. Korkisch, P. Antal and F. Hecht, *ibid.*, 1959, 693.
[64] J. Korkisch and F. Tera, *Analyt. Chem.*, 1961, **33**, 1265.
[65] R. K. Cannan, *J. Biol. Chem.*, 1944, **152**, 401.
[66] R. M. Wheaton and W. C. Bauman, *Ind. Eng. Chem.*, 1951, **43**, 1088.
[67] Ying-Mao Chen, *J. Chinese Chem. Soc. (Taiwan)*, Ser. II, 1955, **2**, 253.
[68] M. Wald and T. Schönfeld, *Monatsh.*, 1958, **89**, 526.
[69] J. Korkisch and A. Farag, *Z. analyt. Chem.*, 1959, **166**, 81.
[70] J. S. Fritz and D. J. Pietrzyk, *Talanta*, 1961, **8**, 143.
[71] L. I. Katzin and E. Gebert, *J. Amer. Soc.*, 1953, **75**, 801.
[72] C. W. Davies and B. D. R. Owen, *J. Chem. Soc.*, 1956, 1676, 1681.
[73] D. G. Tuck and G. A. Welch, *J. Inorg. Nuclear Chem.*, 1959, **9**, 302.
[74] A. Iguchi, *Bull. Chem. Soc. Japan*, 1958, **31**, 600.
[75] *Idem, ibid.*, 1958, **31**, 748.
[76] F. H. Burstall, P. J. Forrest, N. F. Kember and R. A. Wells, *Ind. Eng. Chem.*, 1953, **45**, 1648.
[77] E. W. Berg and J. T. Truemper, *Analyt. Chem.*, 1958, **30**, 1827.
[78] M. Kojima, *Japan Analyst*, 1957, **6**, 369.
[79] *Idem, ibid.*, 1958, **7**, 177.
[80] Y. Yoshino and Y. Kurimura, *Bull. Chem. Soc. Japan*, 1957, **30**, 563.
[81] G. E. Janauer and J. Korkisch, *Talanta*, 1961, **8**, 569.
[82] *Idem, Z. analyt. Chem.*, 1961, **179**, 241.
[83] O. Samuelson and E. Sjöström, *Analyt. Chem.*, 1954, **26**, 1908.
[84] O. Samuelson, E. Sjöström and S. Forsblom, *Z. analyt. Chem.*, 1955, **144**, 323.
[85] R. A. Edge, *J. Chromatog.*, 1961, **5**, 526.
[86] *Idem, ibid.*, 1961, **5**, 539.
[87] L. I. Katzin and J. C. Sullivan, *U.S. Pat.* 2,840,451, June 24, 1958.
[88] N. F. Kember, P. J. MacDonald and R. A. Wells, *J. Chem. Soc.*, 1955, 2273.
[89] O. D. Bonner, *J. Chem. Educ.*, 1957, **34**, 174.

[90] J. Korkisch, Report to International Atomic Energy Agency and U.S. Atomic Energy Commission under contract No 67/US. February 1961.
[91] *Idem., ibid.*, August 1961.
[92] J. Korkisch, P. Antal and F. Hecht, *J. Inorg. Nuclear Chem.*, 1960, **14,** 247.
[93] F. Tera and J. Korkisch, *ibid.*, 1961, **20,** 335.
[94] J. Korkisch and F. Tera, *J. Chromatog.*, 1961, **7,** 564.
[95] P. Antal, J. Korkisch and F. Hecht, *J. Inorg. Nuclear Chem.*, 1960, **14,** 251.
[96] J. Korkisch and F. Tera, *ibid.*, 1960, **15,** 177.
[97] F. Tera, J. Korkisch and F. Hecht, *ibid.*, 1961, **16,** 345.
[98] G. E. Janauer and J. Korkisch, *J. Chromatog.*, 1962, **8,** 516.
[99] J. Korkisch and P. Antal, *Z. analyt. Chem.*, 1959, **171,** 22.
[100] J. Korkisch, P. Antal and F. Hecht, *ibid.*, 1960, **172,** 401.
[101] F. Tera and J. Korkisch, *Analyt. Chim. Acta*, 1961, **25,** 222.
[102] J. Korkisch and F. Tera, *Z. analyt. Chem.*, 1962, **186,** 290.
[103] J. Korkisch and F. Tera, *J. Chromatog.*, 1961, **6,** 530.
[104] F. Helfferich, *Ionenaustauscher*, Band I. Verlag Chemie Weinheim-Germany, 1959.
[105] F. Hecht and W. Reich-Rohrwig, *Monatsh.*, 1929, **53/54,** 596.
[106] Ch. V. Banks and C. H. Byrd, *Analyt. Chem.*, 1953, **25,** 416.
[107] G. E. Janauer and J. Korkisch, *Talanta*, 1962, **9,** 427.
[108] T. Schönfeld, M. El Garhy, C. Friedmann and J. Veselsky, *Mikrochim. Acta*, 1960, 883.
[109] T. Sakaki and H. Kakihana, *Kagaku*, 1953, **23,** 471.
[110] W. C. Waggener and R. W. Staughton, *J. Phys. Chem.*, 1952, **56,** 1.
[111] P. Antal, J. Korkisch and F. Hecht, *Austrian pat.*, No. 219013, June 15th 1961.
[112] G. Arrhenius, J. Korkisch and N. P. Kharkar, In preparation.
[113] G. Arrhenius and J. Korkisch, *Internat. Oceanogr. Congr. Preprints.* Ed. M. Sears, 497. AAAS Wash., C.D., 1959.
[114] F. C. Snell and C. T. Snell, *Colorimetric Methods of Analysis*, 3rd Ed. D. Van Nostrand Company, Inc. Toronto-New York-London, p. 161, 1949.
[115] G. M. Allison, Atomic Energy of Canada, Chalk River, Ontario, PAB-57, 1952.
[116] J. L. Ryan and E. J. Wheelwright, *Ind. Eng. Chem.*, 1959, **51,** 60.
[117] O. D. Bonner and J. C. Moorefield, *J. phys. Chem.*, 1954, **58,** 555.
[118] J. C. Moorefield, Thesis, University of South Carolina, 1953.
[119] J. W. Bodamer and R. Kunin, *Ind. Eng. Chem.*, 1953, **45,** 2577.
[120] F. S. Chance, Jr., G. E. Boyd and H. J. Garber, *ibid.*, 1953, **45,** 1671.
[121] R. W. Gable and H. A. Strobel, *J. phys. Chem.*, 1956, **60,** 513.
[122] H. P. Gregor, D. Nobel and M. H. Gottlieb, *ibid.*, 1955, **59,** 10.
[123] M. H. Gottlieb, Thesis, Polytechnic Institute of Brooklyn, August, 1953.
[124] B. R. Sundheim, M. H. Waxman and H. P. Gregor, *J. phys. Chem.*, 1953, **57,** 974.
[125] C. W. Davies and J. J. Thomas, *J. Chem. Soc.*, 1952, 1607.
[126] O. D. Bonner, *J. Phys. Chem.*, 1954, **58,** 318.
[127] *Idem, ibid.*, 1955, **59,** 719.
[128] H. S. Harned and B. B. Owen, *Physical Chemistry of Electrolytic Solutions.* Reinhold Publ. Corp., New York, N.Y., 1950.
[129] R. M. Fuoss and C. A. Kraus, *J. Amer. Chem. Soc.*, 1933, **55,** 1919, 2387.
[130] D. Reichemberg and W. F. Wall, *J. Chem. Soc.*, 1956, 3364.
[131] K. A. Kraus, F. Nelson and G. W. Smith, *J. phys. Chem.*, 1954, **58,** 11.
[132] S. L. Bafna, *J. Sci. Ind. Res. (India)*, 1953, **12B,** 613.
[133] P. Antal, Thesis, University of Vienna, 1960.
[134] T. V. Arden and G. A. Wood, *J. Chem. Soc.*, 1956, 1596
[135] T. V. Arden and M. Rowley, *ibid.*, 1957, 1709.
[136] D. Kaufman and G. W. Lower, ACCO-68.
[137] E. K. Hyde, *Proceedings Inter. Conference on Peaceful Uses of Atomic Energy* Geneva, 1955, **7,** 281.

Talanta, 1962, Vol. 9, pp. 987 to 995. Pergamon Press Ltd. Printed in Northern Ireland

ANALYTICAL APPLICATIONS OF XYLENOL ORANGE—VI*

A SPECTROPHOTOMETRIC STUDY OF THE NIOBIUM–XYLENOL ORANGE COMPLEX

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Summary—The red niobium-Xylenol Orange complex has been studied spectrophotometrically. It offers a sensitive and selective reaction for the determination of traces of niobium. The coloured complex formed at pH 2·4 to 2·8 by heating in the presence of tartrate has a molar absorptivity of 16,000 and a formation constant of 5×10^6 under the conditions studied. Most metals, including tantalum, vanadium and tungsten, do not interfere when zinc-EDTA complex and tartrate are used as masking agents. Nitrite, oxalate, pyrophosphate, and phosphate interfere. Fluoride can be demasked by addition of beryllium. Platinum gives a dark purple colour which also interferes.

XYLENOL Orange forms a red coloured complex with niobium in a weakly acidic medium.[1] The coloured complex is stable and can be used as a basis for the determination of traces of niobium. The recent excellent review by Elwell and Wood[2] makes it apparent that new, sensitive, and selective methods for niobium are desirable. This paper reports a new, sensitive and selective photometric method for niobium, including the conditions for the colour development of the complex, its composition, its formation constant, and masking effects. It is interesting to point out that tantalum does not undergo any colour reaction with Xylenol Orange and that the interference of titanium, vanadium, molybdenum, and many other metals may be eliminated by zinc-EDTA and tartrate. It seems that Xylenol Orange offers one of the most sensitive and highly selective reactions for niobium (see Table I).

TABLE I.—SENSITIVITY OF SOME COMMON PHOTOMETRIC METHODS FOR NIOBIUM

Method	μg of Nb per cm^2 log $I_0/I = 0{\cdot}001$
Thiocyanate (ethyl ether extraction)	0·0029 (385 mμ)
Thiocyanate (60% v/v acetone)	0·0024 (383 mμ)
Xylenol Orange	0·0058 (535 mμ)
Oxine (chloroform extraction)	0·009 (345 mμ)
Tiron	0·01 (281 mμ)
Hydrochloric acid (12M)	0·01 (281 mμ)
Hydrogen peroxide	0·11 (365 mμ)

EXPERIMENTAL

Apparatus and reagents

Standard niobium solution: A 0·01M stock solution was prepared by fusing 0·1329 g of pure niobium pentoxide with 3 g of potassium pyrosulphate in a platinum crucible, dissolving the melt with 4 ml of concentrated sulphuric acid and 6 ml of water, and making to 100 ml with sulphuric acid and

* Part V: *Talanta*, 1960, **5**, 254.

water after cooling. The solution contained 40 ml of concentrated sulphuric acid in 100 ml. Alternatively, the melt may be dissolved in 50 ml of water containing 10 mmoles of tartaric acid and diluted to 100 ml with water. Appropriate standard niobium solutions, such as $5 \times 10^{-4}M$, were prepared from the stock solution.

1·0*M Tartaric acid*

0·1*M Zinc-EDTA complex solution:* Prepared from pure zinc-ethylenediaminetetra-acetate complex or by mixing appropriate amounts of zinc and the disodium salt of EDTA in water. This solution should contain no significant amounts of free EDTA.

Other apparatus and reagents are the same as those reported previously.[1]

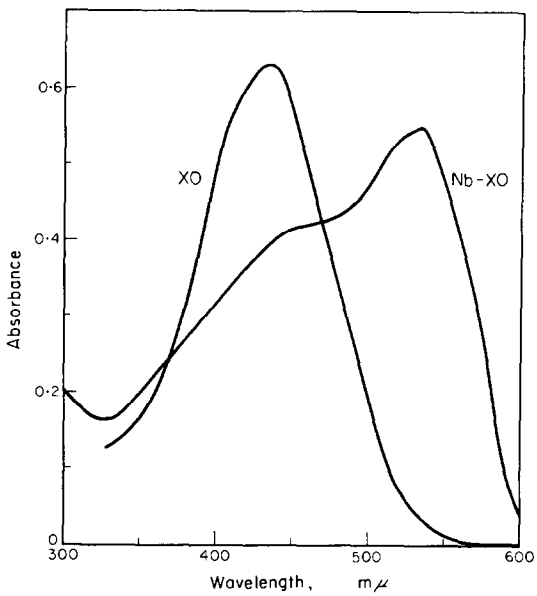


FIG. 1.—Absorption spectra.

Procedure

Calibration curve: Pipette 0 to 4·0 ml of $5 \times 10^{-4}M$ niobium solution into a 100-ml beaker, add 2·0 ml of $1 \times 10^{-3}M$ Xylenol Orange solution, 0·1 mmole of zinc-EDTA, 1 drop of 1·0*M* tartaric acid, and 2·0 ml of 1:1 formic acid. Adjust the pH of the solution to 2·7 and dilute to approximately 15 to 20 ml with water. Cover with a cover glass, heat to boiling on a hot plate for 10 to 15 min, remove and allow to cool to room temperature (do not cool rapidly with cold tap water). After gradual cooling, transfer to a 25-ml volumetric flask and make to volume with water. Measure the absorbance at 535 mμ against a reagent blank. Beer's law is followed. The presence of zinc-EDTA increases the absorbance slightly.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra for Xylenol Orange and its niobium complex are shown in Fig. 1. The maximum absorption for the niobium complex is at 535 mμ.

Effect of pH

A series of solutions containing 2·0 ml of $5 \times 10^{-4}M$ niobium solution, 2·0 ml of $1 \times 10^{-3}M$ Xylenol Orange solution, 0·1 mmole of zinc-EDTA, 1 drop of 1·0*M* tartaric acid, and 2·0 ml of formic acid were prepared. Sodium hydroxide was used for pH adjustment and the colour development was made by boiling and cooling as previously described. The optimum pH range is fairly narrow, the maximum colour development being found to occur at pH 2·4 to 2·8.

Effect of Xylenol Orange

The curve given in Fig. 2 has the same pattern as those previously reported, in that excess of Xylenol Orange tends to decrease the absorbance. Two ml of $1 \times 10^{-3}M$ Xylenol Orange solution are recommended for 0 to 2 μmoles of niobium in 25 ml.

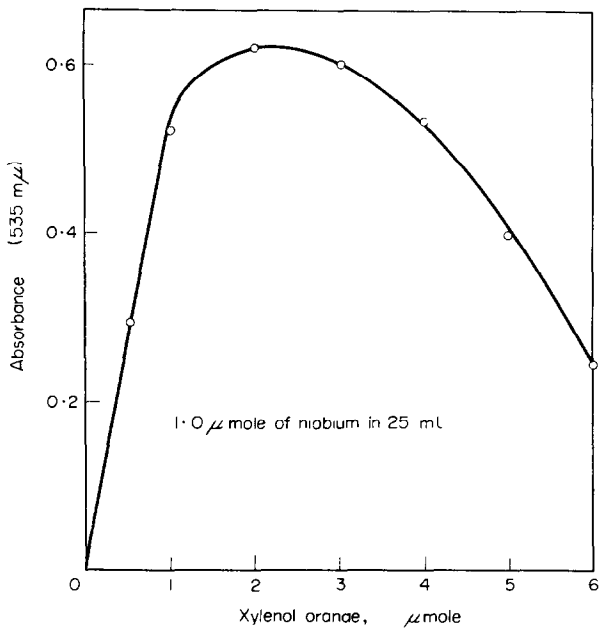


FIG. 2.—Effect of Xylenol Orange.

Effect of temperature

Previously, the colour reaction of niobium and Xylenol Orange was reported to be insensitive,[1] because the test was carried out in the absence of tartaric acid and at room temperature. Later it was reported that niobium gives a sensitive colour reaction with either Xylenol Orange or Methylthymol Blue upon heating in the presence of tartaric acid.[3] By heating for 10 to 15 min there results a linear relationship between the absorbance and temperature below 80°. The absorbance increases slightly at temperatures above 80°, the maximum colour development requiring a temperature of 90 to 100°. It is noted that the maximum colour development also requires a gradual cooling after boiling; therefore, the solution should not be cooled rapidly. Reproducible results were obtained by letting the solution cool at room temperature for 30 min or longer.

Effect of time

It was found that for 1·0 μmole of niobium the boiling time should be longer than 7 min; however, a longer time of boiling does not change the absorbance. It is recommended that the solution be boiled for 10 to 15 min in order to ensure maximum colour development.

Effect of volume

It was noted that irregular absorbancies resulted by using too small or too large a

volume of solution during the boiling period. The optimum volume of the solution during boiling is 15 to 20 ml when 2 ml of $1 \times 10^{-3}M$ Xylenol Orange solution and the specified amounts of other reagents are added.

Effect of tartaric acid and citric acid

The presence of tartaric acid is necessary for the colour development. Apparently, without tartaric acid, niobium is easily hydrolysed at pH 2 to 3; at lower pH values

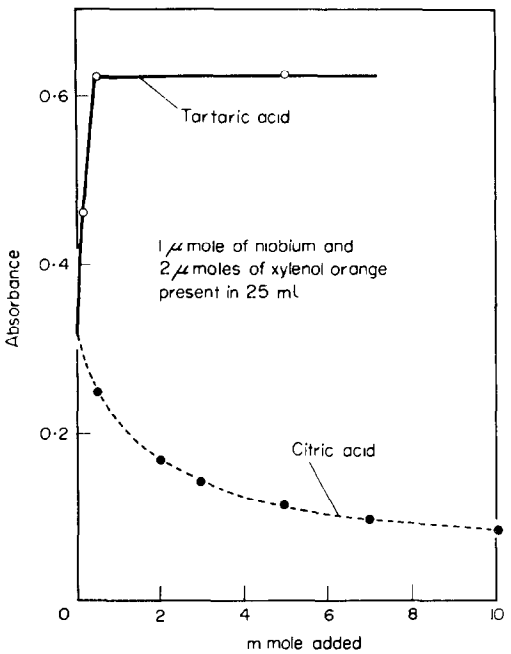


FIG. 3.—Effect of tartaric and citric acids.

niobium cannot compete with protons to form the Xylenol Orange complex. Tartaric acid seems to serve as a solubilising agent to render niobium available for the complex formation; large amounts of tartaric acid do not inhibit the complex formation (see Fig. 3). Citric acid on the other hand inhibits the colour development. It is known that citric acid, in general, is a stronger complexing agent than tartaric acid. The big difference in their behaviour towards the complex formation of niobium and Xylenol Orange is rather surprising.

Effect of EDTA and other complexing agents

As shown in Table II, acetate decreases the absorbance; it is believed that niobium forms a weak complex with acetate. EDTA also decreases the absorbance (Fig. 4). Oxalate, nitrilotriacetic acid (NTA), 1,2-diaminocyclohexanetetra-acetic acid (DCTA), and diethylenetriaminepenta-acetic acid (DTPA) completely prevent the colour development. Niobium has been studied polarographically in an EDTA medium indicating the formation of a niobium–EDTA complex.[5–7] It is surprising that NTA, generally believed a weaker complexing agent compared to EDTA, is more efficient than EDTA in preventing the niobium-Xylenol Orange reaction. It was thought

that addition of a weak metal-EDTA complex might serve as an excellent masking agent to prevent interference from other heavy metals and at the same time give no decrease in absorbance at pH 2 to 3. Manganese^{II}-EDTA and zinc-EDTA were selected and their masking effects are given in Fig. 5. Manganese^{II}-EDTA is not a good masking agent in this case; however, the zinc-EDTA complex is an excellent one.

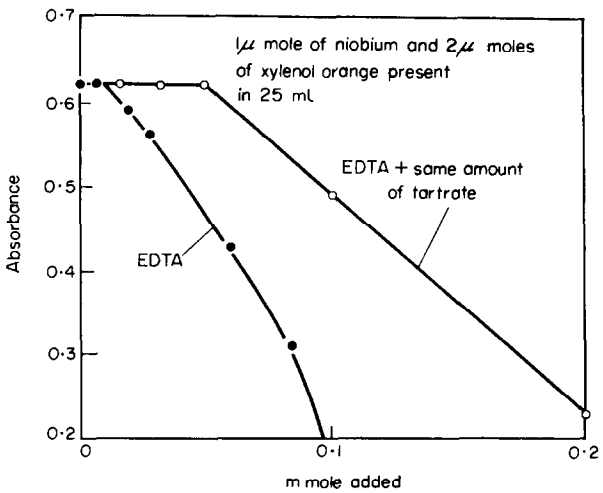


FIG. 4.—Effect of EDTA.

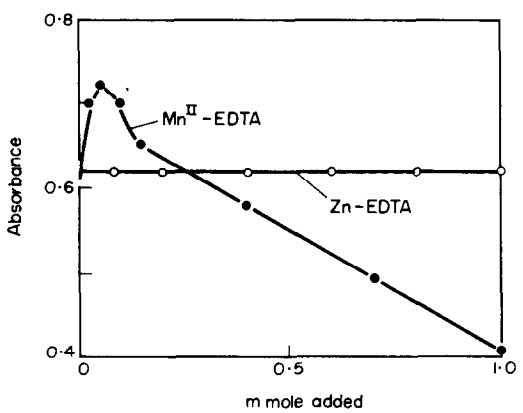


FIG. 5.—Effect of Zn-EDTA and Mn^{II}-EDTA.

This is because manganese^{II}-EDTA is a weaker complex than is the zinc-EDTA complex. The former has an apparent stability constant, $\log K_H = \log K - \log \alpha_H = 16{\cdot}5 - 10{\cdot}5 = 3{\cdot}1$ and the latter $\log K_H = 16{\cdot}5 - 10{\cdot}5 = 6{\cdot}0$, the latter being twice as stable as the former at pH 2·7. At pH 2·7 there is a sufficient amount of free EDTA dissociated from the manganese^{II}-EDTA complex to prevent the niobium-Xylenol Orange reaction. However, many metal ions, such as iron, copper, titanium, bismuth, zirconium, *etc.*, can displace zinc from the zinc-EDTA complex, otherwise these ions would give coloured reactions with Xylenol Orange at pH 2·7. The zinc ion does not give any coloured reaction with Xylenol Orange at a pH below 3; and niobium cannot

displace zinc to form free EDTA. The presence of tartrate prevents the hydrolysis of niobium and allows the toleration of some free EDTA. Addition of very small amounts of manganese^{II}-EDTA to give an "absorption maximum" remains unexplained.

Effect of anions

The effects of many common anions were studied; the results are shown in Table II. Most of the anions do not interfere. Surprisingly, nitrite completely inhibits the colour reaction of niobium and Xylenol Orange; however, no such effect was noticed

TABLE II.—DETERMINATION OF NIOBIUM IN THE PRESENCE OF ANIONS*

Anion Added	*Absorbance*	*Remark*
None	0·860	
Acetate	0·680	
	0·867	1 mmole of acetate; 0·1 mmole of Zn-EDTA and 1 mmole of tartrate added.
Arsenate	0·335	
	0·865	0·05 mmole of arsenate; 0·1 mmole of Zn-EDTA and 1 mmole of tartrate added.
Ascorbic acid	0·864	
Bromide	0·865	
Chloride	0·855	5 mmoles of chloride added.
Fluoride	0·845	2 mmoles of beryllium added.†
Iodide	0·870	
Molybdate	0·855	
Nitrate	0·870	
Nitrite	0·000	
Perchlorate	0·860	
Phosphate	0·480	
	0·848	0·05 mmole of phosphate added; 0·1 mmole of Zn-EDTA and 1 mmole of tartrate added.
Pyrophosphate	0·122	
	0·854	0·05 mmole of pyrophosphate added. 0·1 mmole of Zn-EDTA and 1 mmole of tartrate added.
Sulphate	0·852	10 mmoles of sulphate added.
Vanadate	0·625	0·1 mmole of Zn-EDTA and 1 mmole of tartrate added.
	0·851	0·075 mmole of Zn, 0·1 mmole of Zn-EDTA and 1 mmole of tartrate added.‡
Tungstate	0·865	

* Niobium taken: 1·35 μmoles; anion added: 1 mmole; Zn-EDTA added: 50 μmoles; tartaric acid added: 50 μmoles; volume: 25 ml.

† Fluoride is demasked by beryllium.

‡ The interference of vanadate may be caused by its oxidation of the dye or by its complex formation with niobium or the dye. Addition of free zinc ion is an example of demasking by forming a zinc-vanadate complex.

when nitrite was added to the solution of the pre-formed niobium-Xylenol Orange complex. Large amounts of phosphate, pyrophosphate, arsenate, and traces of fluoride bleach the colour. Except for fluoride, the presence of less than 0·05 mmole of any of the anions does not interfere. Fluoride can be demasked* by addition of beryllium. The effect of acetate can be eliminated by addition of more tartrate (1 mmole). It should be emphasised that large amounts of sulphate and tartrate do not interfere; this is important because they are frequently used in keeping niobium in solution. Vanadate and tungstate do not interfere under the conditions described.

* For a definition of the term "demasking", see K. L. Cheng, *Analyt. Chem.*, 1961, **33**, 783.

Effect of foreign metal ions

Xylenol Orange is a selective reagent in a relatively strong acidic medium; above pH 2·5 many metal ions give coloured reactions with Xylenol Orange. In order to increase its selectivity, suitable masking agents must be used. Most common metal ions do not interfere if zinc-EDTA and tartrate are added, as shown in Table III. Cerium^{IV} interferes because of its oxidising ability, but cerium^{III} does not. The interference of platinum^{IV} could not be masked by zinc-EDTA and tartrate. Tantalum and tin do not interfere.

TABLE III.—DETERMINATION OF NIOBIUM IN THE PRESENCE OF FOREIGN METALS.*

Metal Added	*Absorbance*	*Remark*
None	0·860	
Al	0·868	0·2 mmole of Zn-EDTA and 1 mmole of tartrate added
Sb^{III}	0·858	
Bi	0·860	
Cd	0·860	
Ca	0·865	
Ce^{III}	0·470	
	0·850	0·1 mmole of Zn-EDTA and 1 mmole of tartrate added
Co^{II}	0·865	
Cu^{II}	0·853	
Ga	0·850	
Hf	0·855	
In	0·860	
Fe^{III}	0·858	
La	0·863	
Pb^{II}	0·864	
Hg^{II}	0·856	
Ni	0·700	
	0·720	0·1 mmole of Zn-EDTA and 0·05 mmole of tartrate added
	0·865	0·1 mmole of Zn-EDTA and 1 mmole of tartrate added
Pt^{IV}	0·700	0·1 mmole of Zn-EDTA and 1 mmole of tartrate added; Pt forms a dark purple colour with Xylenol Orange.
Ag^{I}	0·880	
Ta	0·850	0·1 mmole of Ta added; 0·1 mmole of Zn-EDTA and 1 mmole of tartrate added.
Th	0·850	
Sn^{IV}	0·800	
	0·865	1 mmole of tartrate added
Ti^{IV}	1·50	
	0·870	0·2 mmole of Zn-EDTA added
UO_2^{II}	0·852	
Zr	0·858	

* Niobium taken: 1·35 μmoles; foreign metal added: 10 μmoles; Zn-EDTA added: 50 μmoles; tartaric acid added: 50 μmoles; Volume: 25 ml.

Complex formation

It is difficult for niobium to react directly with Xylenol Orange, but it readily forms a coloured complex with Xylenol Orange upon heating in the presence of tartrate, which likely acts as a carrier.

Niobium forms chiefly a 1:1 complex with Xylenol Orange, as indicated by Job's method (Fig. 6). The formation constant was calculated from the curves in Fig. 6 based on the method used previously.[4] It was found to be $5{\cdot}0 \times 10^6$ at pH 2·5. Because of its relatively low stability, it is easily understood why oxalate, pyrophosphate, phosphate and fluoride can bleach the colour reaction of niobium and Xylenol Orange.

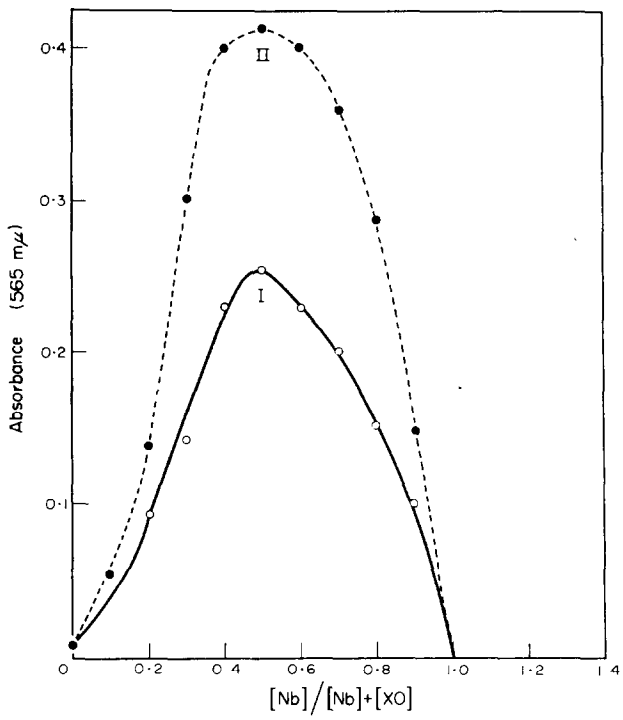
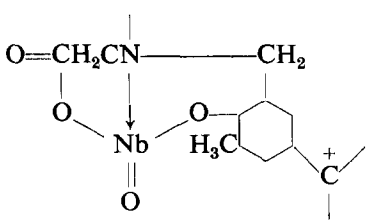


FIG. 6.—Job's curve.
I—Total concentration of niobium and Xylenol Orange = $4 \times 10^{-5}M$.
II—Total concentration of niobium and Xylenol Orange = $8 \times 10^{-5}M$.

Niobium has a tendency to form stable complexes with compounds having β-diketo, carboxylic acid, or phenolic groups. Therefore, it is believed that the phenolic, amine, and carboxylic groups of Xylenol Orange are involved in the chelation:



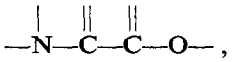
Methylthymol Blue, an analogue of Xylenol Orange, behaves similarly towards niobium, forming a red coloured complex upon heating in a weakly acidic medium in the presence of tartrate. That 3,3′-bis-[N,N-di(carboxymethyl)aminomethyl]thymolphthalein (Methylthymol Blue without the sulphonate group) gave no coloured reaction with niobium is not understood, at present.

For future synthesis of new colorimetric reagents for niobium, the present results suggest that replacement of the methyl group with a hydroxyl or carboxylic group on the phenolic ring of Xylenol Orange may result in more sensitive or more stable colorimetric reagents for niobium.

Just as with Xylenol Orange and Methylthymol Blue, it has been found that niobium reacts with 1-(2-pyridylazo)-2-naphthol (PAN) or with 4-(2-pyridylazo)-resorcinol

(PAR) at pH 2·5–3·0, on heating in the presence of tartaric acid, giving a sensitive red colour. The selectivity of these reactions can also be improved by adding Zn-EDTA.

It is interesting to note that the four dyes contain a common grouping,



and that the same conditions for its formation apply. The Nb-PAN complex can be extracted by isoamyl alcohol.

Zusammenfassung—Der rote Niob-Xylenol Orange-Komplex wurde spectrophotometrisch untersucht. Der Komplex bietet die Grundlage für eine empfindliche und selektive Bestimmung von Spuren von Niob. Der Komplex bildet sich bei pH 2·4–2·8 in Gegenwart von Tartrat unter Erwärmen und hat einen molaren Absorptionskoeffizienten von 16,000. Die Stabilitätskonstante unter den gegebenen Bedingungen ist 5.0×10^6. Die meisten Metalle, einschliesslich Ta, V und W stören nicht, wenn Zn-ÄDTE und Tartrat als Maskierungsmittel zugesetzt werden. Fluorid, Nitrit, Oxalat, Pyrophosphat und Phosphat stören. Platin gibt eine dunkle Purpurfärbung und stört ebenfalls.

Résumé—Les auteurs ont étudié par spectrophotométrie le complexe rouge niobium-orangé de xylénol. Ce composé donne une réaction sensible et sélective pour le dosage de traces de niobium. Le complexe coloré formé par chauffage à pH 2,4–2,8 en présence de tartrate a une absorption molaire de 16.000 et une constante de formation de $5,0 \times 10^6$ dans le conditions étudiées. La plupart des métaux, dont le tantale, le vanadium et le tungstène ne gênent pas si on utilise le complexe zinc-EDTA et le tartrate comme agents complexants. Le fluorure, le nitrite, l'oxalate, le pyrophosphate et le phosphate gênent. Le platine donne une coloration pourpre foncée et gêne.

REFERENCES

[1] K. L. Cheng, *Talanta*, 1959, **2**, 61.
[2] W. T. Elwell and D. F. Wood, *Analyt. Chim. Acta*, 1962, **26**, 1.
[3] K. L. Cheng, Lecture at XVIIIth International Chemical Congress, August, 1961, Montreal, Canada.
[4] *Idem*, *Talanta*, 1959, **2**, 266.
[5] D. J. Ferrett and G. W. C. Milner, *J. Chem. Soc.*, 1956, 1186.
[6] *Idem*, *Nature*, 1955, **175**, 477.
[7] J. H. Kennedy, *Analyt. Chem.*, 1961, **33**, 943.

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UNTERSUCHUNGEN ÜBER DIE REAKTIONSFÄHIGKEIT VON CHROM UND TITAN MIT PYRROLIDINDITHIOCARBAMINAT

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Zusammenfassung—Es wird die Reaktionsfähigkeit von Titan in Abhängigkeit vom pH-Wert der Lösung und anderer anwesender Anionen und die Reaktionsfähigkeit von Chrom in Abhängigkeit von dem Bindungszustand des Chrom(III)-Ions und dem pH-Wert der Lösung jeweils mit Pyrrolidindithiocarbaminat untersucht. Die gewonnen Ergebnisse geben eine Erklärung für die zur Zeit sehr unterschiedlichen Beschreibungen der Reaktionsfähigkeit der beiden Metalle Chrom und Titan mit disubstituierten Dithiocarbaminaten.

EINLEITUNG

DAS Studium der Literatur zeigt, daß bezüglich der Reaktion von Chrom bzw. Titan mit disubstituierten Dithiocarbaminaten sehr unterschiedliche Ansichten bestehen.

Titan

In Übereinstimmung mit der zeitlich vorhergehenden Literatur führt der eine von uns[1] 1955 an, daß das Titanion keine Reaktion mit einer Pyrrolidindithiocarbaminatlösung eingehe. Darauf aufbauend wurde eine Methode entwickelt,[2] die es ermöglicht, mit Hilfe von Pyrrolidindithiocarbaminat Schwermetalle in Eisen und Eisenerzen quantitativ von Titan abzutrennen. O. G. Koch[3] beschreibt eine Abtrennung der Schwermetalle von Titan in Titanmetall und Titanlegierungen auf dieselbe Weise. Demgegenüber stehen die Bericht von Rooney[4,5] aus 1958, denen zufolge eine Titandiäthyldithiocarbaminat-Verbindung besteht, die er sogar beschränkt dazu auswerten konnte, um im Gußeisen eine positive Trennung Titan von geringen Mengen Aluminium durchzuführen.

In der Tatsache allein, daß einerseits Diäthyldithiocarbaminat, andererseits Pyrrolidindithiocarbaminat verwendet wurde, ist nicht von vornherein eine Erklärung des Widerspruches zu suchen, da übereinstimmend aus sämtlichen Literaturangaben hervorgeht, daß sich die einzelnen Carbaminate nicht prinzipiell in iherm Verhalten verschiedenen Kationen gegenüber unterscheiden, sondern daß Differenzierungen nur im mengenmäßigen Ausmaß und in der Geschwindigkeit der Reaktionen liegen.

Chrom

Auch über die Fällbarkeit des Chroms bestehen zwei Ansichten. Malissa und Mitarbeiter[6] führen eine Chromdiäthyl-, sowie eine Chrompyrrolidindithiocarbaminatverbindung an, während Bode[7] für Diäthyldithiocarbaminat im pH-Bereich 4–11 keine Reaktion mit Chrom feststellen konnte, allerdings setzte er für seine Versuche

Kaliumchromalaun ein. Nach Gleu und Schwab[8] ist die Bildung der Chrompyrrolidindithiocarbaminatverbindung erst dann quantitativ, wenn man die Reaktion bei einem pH-Wert von 5 bei etwa 70°C mit Überschuß des Fällungsmittels durchführt und anschließend auch noch aufkocht.

VERSUCHE ZUR FÄLLUNG DES TITANS UND DES CHROMS MIT PYRROLIDINDITHIOCARBAMINAT

Titan

Versetzt man eine Titanylsulfatlösung von pH 1 mit einer 10%igen, wässrigen Pyrrolidindithiocarbaminatlösung, so tritt eine weiße Fällung auf, bestehend aus der freien Pyrrolidindithiocarbaminsäure. Puffert man aber die stark saure Lösung schrittweise mit Acetatpuffer, so zeigt sich bis pH 5keine Fällung einer gelben Pyrrolidindithiocarbaminatverbindung (Fällung rein weiß), im pH-Bereich 5 bis 6 jedoch wird der gefallene Niederschlag gelblich, wahrscheinlich zurückzuführen auf teilweise Mitfällung einer Titan-Pyrrolidindithiocarbaminatverbindung zusammen mit der freien Pyrrolidindithiocarbaminsäure.

Geht man umgekehrt vor, daß man nämlich die saure Lösung des Titanylsulfates zur ungepufferten, schwach alkalischen Pyrrolidindithiocarbaminatlösung hinzufügt, so erhält man einen grobflockigen gelborange gefärbten Niederschlag. Fügt man dazu nun 10%ige Schwefelsäure bis zur Erreichung eines pH-Wertes von 0, so kann man keine sichtbare Zerstörung der Fällung beobachten. Kocht man die das Titanpyrrolidincarbaminat enthaltende Lösung jedoch auf, so wird es sofort zerstört. In Chloroform ist die Verbindung ausgezeichnet löslich, doch zeigt sich, daß eine derartige Lösung, die anfänglich intensiv gelborange gefärbt ist, bei 1–2 stündigem Stehen vollkommen farblos wird, also nicht vorteilhaft für photometrische Zwecke geeignet ist.

Die Analyse der oben erwähnten gelborange gefärbten Titanpyrrolidindithiocarbaminatverbindung ergab:

	gefunden	theoret. bei Annahme einer $Ti(Carb)_3$
C	45,7–45,8%	37,1%
S	30,2–30,9%	39,5%
Ti	1,2– 1,5%	9,88%

Es ist noch zu untersuchen, um welche Verkettung des Titans mit dem Carbaminat es sich hiebei handelt bzw. ob es sich nicht nur um ein mit der freien Carbaminsäure bzw. deren Zersetzungsprodukten verunreinigtes Produkt handelt.

Je nach dem Verhältnis der Mengen an Titan und Pyrrolidindithiocarbaminat gelang es, durch einmalige Fällung größere oder kleinere Mengen Titan als „Titanpyrrolidindithiocarbaminat" abzuscheiden. Selbst bei 10 fachen Überschuß des Fällungsmittels, bezogen auf die theoretisch notwendige Menge, war es aber nicht möglich, in einem Schritt eine vollständige Abscheidung zu erzielen. Es lag nun nahe, anzunehmen, daß der pH-Wert eine entscheidende Rolle bei der Fällung des „Titanpyrrolidindithiocarbaminates" spiele, abgeschen vom Einfluß großen Fällungsmittelüberschusses.

Fällungsversuche in stark acetatgepufferten Titanylsulfatlösungen waren jedoch im pH-Bereich 1–6 weder dann erfolgreich, wenn die titanhältige Lösung mit dem Carbaminat versetzt wurde, noch, wenn umgekehrt vorgegangen wurde. Damit ist

gezeigt, daß für die Fällbarkeit einer Titanpyrrolidindithiocarbaminatverbindung primär der Einfluß der Acetationen wichtig ist. Das erklärt sich zwangslos daraus, daß Titanionen große Neigung zur Bildung von Komplexverbindungen besitzen, die so stabil sind, daß sie nicht mehr auf Pyrrolidindithiocarbaminat ansprechen. Bekannt ist beispielsweise, daß selbst die Bildung des sehr beständigen Peroxodisulfatotitansäurekomplexes durch Anwesenheit großer Mengen an Acetationen teilweise unterbunden wird.

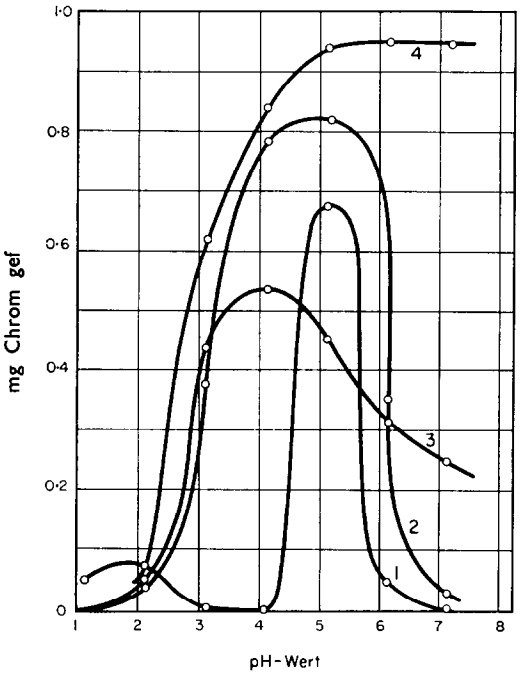


Abb. 1.—Abhängigkeit der Chrompyrrolidindithiocarbamatfällung vom pH-Wert
1—sofort titriert (A): 2—nach 16 Stunden (C):
3—nach 2 Stunden (B): 4—pH-Wert auf Ausgangswert zurückgebracht.

Der pH-Wert wurde nun der Reihe nach mit Natriumcitrat-, Glykokoll- und Urotropinpuffer variiert. In keinem Fall konnte eine „Titanpyrrolidindithiocarbaminatfällung" erzielt werden. Erst bei sehr wenig Puffersubstanz trat teilweise Fällung auf.

Diese Zusammenhänge lassen die Widersprüche, die betreffs der Bildung einer „Titanpyrrolidindithiocarbaminatverbindung" herrschen, von einer anderen Warte her betrachten. Malissa[1] und Koch[3] arbeiteten jeweils in stark acetatgepufferten Lösungen und erhalten in Übereinstimmung mit obigen Versuchen keinerlei Fällung des Titans. Rooney[4] beschreibt die Fällung erstens aus mit Glykokoll gepufferter Lösung und zweitens führt er an, daß nur so viel Puffer angewendet wurde, um eben den pH-Wert während des Vorganges konstant zu halten (Nähere Angaben fehlen).

Im allgemeinen ist zu ersehen, daß Titan nur eine geringe Affinität bezüglich Pyrrolidindithiocarbaminat besitzt und es daher nur unter Einhaltung ganz spezieller Bedingungen zur noch nicht geklärten Reaktion gebracht werden kann.

Chrom

Ausgehend von einer Kaliumdichromatlösung wurde durch Reduktion mit Salzsäure und Wasserstoffperoxid eine Chrom(III)-haltige Lösung hergestellt. Von dieser Stammlösung (1 ml = 1 mg Cr) wurden 2 ml abpipettiert, mit 2 ml 20%iger Weinsäurelösung und 1 ml 50%iger Ammonacetatlösung versetzt und auf den jeweiligen pH-Wert eingestellt. Die Lösung wurde erwärmt und mit 2 ml 10%iger Natriumpyrrolidindithiocarbaminatlösung versetzt. Den hiebei ausgefallenen Niederschlag ließ man einige Zeit in der Wärme (60°C) absitzen und filtrierte dann ab. Nach Auflösung in Salpetersäure (1 + 1) wurde die Lösung fast bis zur Trockene eingedampft; und, um das Carbaminat restlos zu zerstören noch zweimal mit Salpetersäure, der etwas Wasserstoffperoxid zugesetzt war, aufgenommen und eingedampft. Hienach gab man nochmals etwas Wasserstoffperoxid zu und machte die Lösung mit NaOH alkalisch. Aus dieser Lösung wurden aliquote Teile nach dem Diphenylcarbazidverfahren auf Chrom untersucht.

TABELLE I.—FÄLLBARKEIT DES CHROMS ALS CHROMPYRROLIDINDITHIOCARBAMINAT IN ABHÄNGIGKEIT VOM pH-WERT DER LÖSUNG UND DER ABSETZZEIT

	Absetzzeit		
pH	A	B	C
1	0,052	0,003	0,002
2	0,007	0,049	0,039
3	0,001	0,440	0,381
4	0,001	0,545	0,787
5	0,686	0,400	0,825
6	0,055	0,320	0,355
7	0,001	0,253	0,035

Filtriert man sofort nach der Zugabe von Pyrrolidindithiocarbaminat und dem Aufkochen der Lösung ab (A), so erhält man bei Bestimmung des Chroms im verbliebenen Rückstand stark streuende Werte, die bei pH 5 ein Maximum zeigen. Läßt man hingegen 2 Stunden stehen (B), so nimmt die Zerstörung des anfangs gebildeten Chrompyrrolidindithiocarbaminates im stark sauren Bereich zu. Ab pH 3 macht sich jedoch schon die stabilisierende Wirkung des abgespaltenen Natriumions aus dem Carbaminat bemerkbar, indem es zu einer höheren Chrompyrrolidindithiocarbaminatausbeute führt, die ebenfalls zwischen pH 4 und 5 ihren Höchstwert hat. Nach sechzehnstündigem Stehenlassen (C) sind diese Effekte noch stärker ausgeprägt, ohne aber den Sollwert (1 mg) zu erreichen.

Da Messungen des pH-Wertes bei Versuchslösungen im pH-Bereich von 1–4 knapp vor der Filtration zeigten, daß eine Verschiebung des ursprünglichen Wertes zum Neutralpunkt hin erfolgt, wurden in einer weiteren Versuchsreihe sofort nach der Fällung die pH-Werte wieder auf ihren anfänglichen Wert zurückgebracht und dann noch zwei Stunden absitzen gelassen.

Tabelle II zeigt, daß bei den vorher angegebenen Bedingungen bei pH 1 Chrompyrrolidindithiocarbaminat praktisch nicht beständig ist, während ansonsten mit

TABELLE II.—FÄLLBARKEIT DES CHROMS ALS PYRROLIDINDITHIOCARBAMINAT IN ABHÄNGIGKEIT VOM pH-WERT DER LÖSUNG

pH	mg Cr gefunden
1	—
2	0,076
3	0,621
4	0,840
5	0,941
6	0,950
7	0,952

steigendem pH-Wert ein kontinuierliches Ansteigen der Chrompyrrolidindithiocarbaminatausbeute zu erkennen ist.

Weiters wurde eine Chrom(III)-haltige Lösung aus Kaliumchromalaun hergestellt und mit 10%iger Pyrrolidindithiocarbaminatlösung zu fällen versucht. Im pH-Bereich 2 bis 6 konnte keine Chrompyrrolidindithiocarbaminatfällung beobachtet werden. Es ist also zweifellos so, daß die Fällbarkeit oder die Nichtfällbarkeit eines Chrom(III)pyrrolidindithiocarbaminates stark von den jeweiligen Zustandsbedingungen des Metallions abhängig ist. Nur auf diese Weise kann verstanden werden, wie Bode[7] einerseits und Malissa[6] andererseits zu den bereits besprochenen verschiedenen Ansichten kommen konnten.

Chromatlösungen reagieren in der Kälte mit Pyrrolidindithiocarbaminat bei pH 2 bis 5 nicht. Erhitzt man jedoch auf ca. 70°C und versetzt mit großem Überschuß des Fällungsmittels, so zeigt sich anfänglich eine graublaue Trübung, die sich bei längerem Stehen verstärkt. Es wurde nun versucht, eine Fällung derart zu begünstigen, daß eine halbe Stunde lang kräftig umgeschüttelt wurde. Es zeigte sich, daß so eine Niederschlagsbildung erreicht werden kann. Die Filtration lieferte eine relativ feinkörnige graublaue Substanz, im Filtrat jedoch konnten noch große Mengen sechswertigen Chroms nachgewiesen werden. Der nicht vollständig gebildete Niederschlag dürfte zufolge seines Aussehens aus Chrom(III)pyrrolidindithiocarbaminat bestehen, dessen Bildung folgendermaßen zu verstehen ist. Sechswertiges Chrom wurde vorerst durch das Fällungsmittel zu dreiwertigem reduziert und dieses bildete dann allmählich im Laufe seines Entstehens die bekannte Chrom(III)pyrrolidindithiocarbaminatverbindung.

Summary—The dependence of the reactivity with pyrrolidinedithiocarbamate of titanium on pH and the presence of other ions, and of chromium^{III} on the state of binding of the chromium^{III} ion and on pH have been investigated. The results of this investigation provide an explanation of the hitherto very variable accounts of the reactivity of titanium and chromium with disubstituted dithiocarbamates.

Résumé—Les auteurs étudient l'influence du pH et de la la présence d'autres ions sur le pyrrolidinedithiocarbamate de titane et l'influence du pH et de l'état sous lequel se trouve le chrome (III) en solution sur le pyrrolidinedithiocarbamate de chrome (III). Les résultats obtenus permettent d'expliquer les différences rencontrées quant aux réactions du chrome et du titane avec les dithiocarbamates bisubstitués.

LITERATUR

[1] H. Malissa, F. Wever u. W. Koch, *Forsch. Ber. d. Wirtsch.-u. Verkehrsmin. Nordrhein Westfalen*, Nr. 229. Westd. Verlag Köln-Opladen, 1955.
[2] H. Malissa u. E. Schöffmann, *Arch. Eisenhüttenw.*, 1957, **28**, 623.
[3] O. G. Koch, *Mikrochim Acta*, 1955, **1**, 151.
[4] R. C. Rooney, *Analyt. Chim. Acta*, 1958, **19**, 428.
[5] *Idem*, *Analyst*, 1958, **83**, 546.
[6] H. Malissa u. E. Schöffmann, *Mikrochim. Acta*, 1955, **1**, 188.
[7] H. Bode, *Z. analyt. Chem.*, 1955, **144**, 165.
[8] K. Gleu u. R. Schwab, *Angew. Chem.*, 1950, **62**, 320.
[9] E. E. Kotlyar u. T. N. Natarchuk, *Zhur. Anal. Khim.* 1961 **19**, 688.

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THERMOGRAVIMETRY OF SOME URANIUM^{VI} 8-HYDROXYQUINOLATES

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Summary—The thermogravimetric behaviour of
$UO_2(C_9H_6NO)_2.C_9H_6NOH$ and $[UO_2(C_9H_6NO)_2]_2.C_9H_6NOH$
prepared by precipitation from homogeneous solution with 8-acetoxyquinoline has been found to closely resemble that of
$UO_2(C_9H_6NO)_2.C_9H_6NOH$
prepared by direct precipitation of uranium^{VI} with 8-hydroxyquinoline.

PREVIOUS thermogravimetric studies have been made by Duval[1] and by Wendlandt[2] with uranium 8-hydroxyquinolate prepared by conventional precipitation.[3] Duval found the precipitate to be thermally stable up to 157°. The molecule of crystallisation was removed above this temperature; an apparently stable quinolate, UO_2Q_2 (where $Q = C_9H_6NO$), exists in the range 252–346°. Beyond 346°, Duval's thermogram showed a rapid weight loss up to about 400°, followed by a slower loss that continued up to 947° which was the upper limit of the thermal analysis made by him. The subsequent investigation by Wendlandt[2] indicated that the unsolvated chelate began to decompose at 380°, that conversion to the oxide U_3O_8 was complete at 450°, and that no further weight loss occurred above this temperature. Neither author specified the heating rate that was used in the pyrolysis, but differences in this variable would not account for the marked discrepancy between their results above 400°.

The present paper describes thermogravimetric studies made with uranium 8-hydroxyquinolates precipitated from homogeneous solution with 8-acetoxyquinoline[4] at two different pH levels; the two precipitates formed appear to have the compositions $UO_2Q_2{\cdot}HQ$ and $(UO_2Q_2)_2{\cdot}HQ$. The thermogravimetric behaviour of the conventionally formed precipitate, *i.e.*, $UO_2Q_2{\cdot}HQ$ produced by 8-hydroxyquinoline, was also examined for comparative purposes.

EXPERIMENTAL

Preparation of precipitates for thermogravimetric analysis

The precipitates of uranium 8-hydroxyquinolate were prepared in accordance with the described procedures.[3,4] After the precipitates were washed and dried at 110° for 2 hr, they were weighed in order to confirm quantitative precipitation.

Thermogravimetric procedure

Approximately 100-mg portions of the precipitate, prepared as described, were transferred to crucibles freshly ignited at 850° and subsequently briefly stored in a desiccator. The samples were then subjected to a heating rate of 6°/min or 1°/min in a Stanton HTD thermobalance. Except where indicated, an air atmosphere was used. All data used in the preparation of the thermogravimetric curves in the following figures were corrected for buoyancy (experimentally determined for each crucible).

In some instances the heating programmes were interrupted in order to maintain a constant temperature for specified time periods.

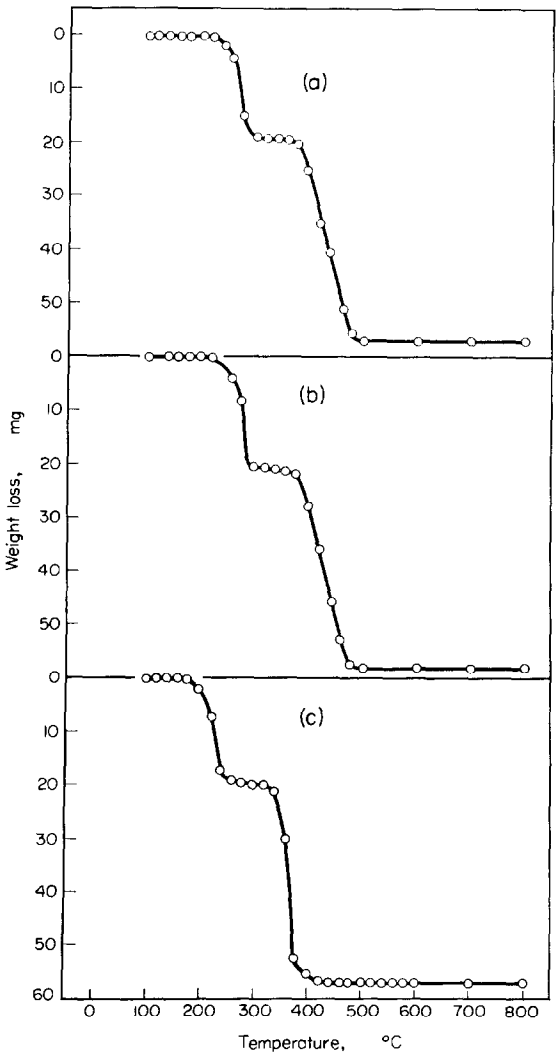


FIG. 1.—Thermogravimetric curves of uranium^{VI} 8-hydroxyquinolate:
(a) UO_2Q_2·HQ prepared by conventional precipitation (heating rate: 1°/min; sample size: 96·2 mg).
(b) UO_2Q_2·HQ prepared by PFHS (heating rate: 1°/min; sample size: 97·3 mg).
(c) $(UO_2Q_2)_2$·HQ prepared by PFHS (heating rate: 1°/min; sample size: 99·7 mg).

RESULTS AND DISCUSSION

Weight loss-temperature data are shown in Fig. 1, respectively, for UO_2Q_2·HQ prepared by conventional precipitation, UO_2Q_2·HQ prepared by PFHS (precipitation from homogeneous solution) at pH 5·0, and $(UO_2Q_2)_2$·HQ prepared by PFHS at pH 6·8; Fig. 2 shows the weight loss-time data of UO_2Q_2·HQ held at 320° for many hr.

Thermogravimetric behaviour of UO_2Q_2·HQ *prepared by PFHS and by conventional precipitation*

Precipitates prepared by PFHS and by conventional precipitation were found to behave in a quite similar manner for they were thermally stable up to about 200° [*cf.*

Figs. 1(a) and 1(b)]. Between 200° and 300°, the two precipitates apparently lost their molecules of crystallisation. The remaining organic material disappeared between 375° and 475° to form U_3O_8 which was stable above 500° and up to the 1200°-level to which the furnace was occasionally operated. The thermal behaviour of the conventionally formed precipitate (as well as that prepared by PFHS) agreed quite closely with Wendlandt's but not with Duval's observations. A quantitative analysis of several thermogravimetric curves is shown in Table I and indicates uncertainty in using UO_2Q_2 as a weighing form (in air) for the determination of uranium; in making the

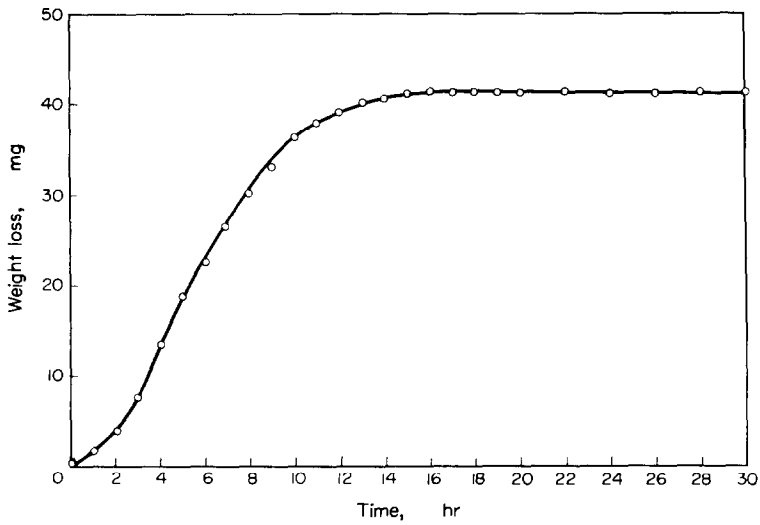


FIG. 2.—Weight loss of UO_2Q_2·HQ at constant temperature (320°; sample size: 124·5 mg).

analyses for UO_2Q_2, the mid-points of the "plateaus" were used. There is also some uncertainty associated with U_3O_8 but in view of the horizontal nature of the final plateau, further work would be required to warrant any conclusion about the use of U_3O_8 as a weighing form in the present case. However, as shown in a previous investigation,[4] drying of the precipitate at 110°, *i.e.* the weighing form UO_2Q_2·HQ, leads to quite satisfactory results.

TABLE I.—QUANTITATIVE ANALYSIS OF THERMOGRAVIMETRIC CURVES OF UO_2Q_2·HQ

Sample weight, *mg*	96·2	97·3	68·6
Method of precipitation	Conventional	PFHS pH = 5·0	PFHS pH = 5·0
Heating rate of sample, °*C/min*	1	1	6
Weight loss for intermediate plateau, *mg*			
Observed	19·6	20·4	13·6
Theory[a]	19·8	20·1	14·2
Weight loss for final plateau, *mg*			
Observed	38·0	38·1	25·9
Theory[b]	38·0	38·4	27·0

[a] UO_2Q_2·HQ → UO_2Q_2 + HQ
[b] $3UO_2Q_2$ → U_3O_8 + degradation products

Because of the presence of a non-horizontal "plateau" in the 300–375° region, the compounds obtained in this temperature range were further examined both by an alteration in the thermogravimetric technique and by bromination[5] to determine their 8-hydroxyquinoline content; only precipitates prepared by PFHS were brominated.

The heating programme was altered so that the temperature remained constant once 320° was reached; the choice was arbitrary although it can be seen from Figs. 1(a) and 1(b) that 320° is within a "plateau" region. The *orange* coloured precipitate prepared by PFHS (pH 5·0) slowly lost weight for about 18 hr after the 320°-level was reached. No weight loss was observed for the next 12-hr period as is shown by Fig. 2. The resulting *yellow* precipitate was analysed for carbon, nitrogen, hydrogen and uranium. Because UO_3 is yellow and U_3O_8 is dark olive drab (almost black), it was at first thought that the yellow compound was UO_3. However, the compound appeared to be a mixture of a uranium oxide and organic degradation products. The results are shown in Table II. Similar results were obtained with $UO_2Q_2 \cdot HQ$ prepared by conventional precipitation.

TABLE II.—ELEMENTAL COMPOSITION OF THE YELLOW URANIUM COMPOUND OBTAINED UPON PROLONGED HEATING AT 320°

Element	N	H	C	U
Theory for UO_2Q_2, %	5·0	2·1	38·7	42·6
Observed[a], %	0·44	0·68	1·66	78·8[b]

[a] The initial sample of $UO_2Q_2 \cdot HQ$ taken weighed 30·5 mg; the weight of yellow compound taken for microanalysis was 5·3 mg.
[b] Theory for U in UO_3 = 83·2%

When the previous experiment was repeated at two other temperatures, *i.e.*, at 260 and at 300°, different rates of weight loss were obtained although the overall results were essentially similar to those obtained at 320°.

In similar experiments, with several temperatures in the range 280–360°, the compounds obtained were also analysed by bromination for their 8-hydroxyquinoline content. The results in Table III show a continual variation, with temperature, of the

TABLE III.—APPROXIMATE COMPOSITION OF URANIUM COMPOUND OBTAINED IN 280–360° TEMPERATURE RANGE

Temperature, °C	280	300	320	340	360
Mole Ratio: $\frac{\text{8-hydroxyquinoline}}{\text{uranium}}$	2·20, 2·29	1·88, 1·92	1·50, 1·73	1·26 ,1·59	1·33, 1·49

mole ratio of 8-hydroxyquinoline to uranium. It is apparent that data obtained from the first thermogravimetric "plateau" cannot be used for the quantitative determination of uranium (weighed as UO_2Q_2) if the precipitate is heated in an air atmosphere where oxidation can occur.

When a nitrogen atmosphere was used, the compound did not lose weight when heated for a 20-hr period at 320°. The gravimetric data indicated the stable compound to be UO_2Q_2; the initial sample of $UO_2Q_2 \cdot HQ$ which weighed 117·5 mg was observed to lose 24·2 mg in agreement with the theoretically expected loss of 24·2 mg.

$(UO_2Q_2)_2 \cdot HQ$ *Prepared by PFHS at* pH 6·8

The thermogravimetric curve shown in Fig. 1(c) for $(UO_2Q_2)_2 \cdot HQ$ is quite similar to that of Fig. 1(b) for $UO_2Q_2 \cdot HQ$. In addition, the weight loss-time curve for $(UO_2Q_2)_2 \cdot HQ$ was almost identical with that obtained for $UO_2Q_2 \cdot HQ$ at the 320°-level (*cf.* Fig. 2).

The data obtained from the middle of the "plateaus" of thermograms for $(UO_2Q_2)_2 \cdot HQ$ were not sufficiently accurate for gravimetric purposes (except at 110° as shown in the previous investigation[4]) for either UO_2Q_2 or U_3O_8 as weighing forms as is shown in Table IV (*cf.* with Table I). It is difficult from the data of Tables I and IV to determine

TABLE IV.—QUANTITATIVE ANALYSIS OF THERMOGRAVIMETRIC CURVES OF $(UO_2Q_2)_2 \cdot HQ$

Sample weight, *mg*	87·9	99·7
Method of precipitation	PFHS pH = 6·8	PFHS pH = 6·8
Heating rate of sample, *°C/min*	1	1
Weight loss for intermediate plateau, *mg*		
Observed	16·0	19·5
Theory[a]	10·1	11·5
Weight loss for final plateau, *mg*		
Observed	31·7	37·5
Theory[b]	38·7	43·9

[a] $(UO_2Q_2)_2 \cdot HQ \rightarrow 2UO_2Q_2 + HQ$
[b] $3(UO_2Q_2)_2 \rightarrow 2U_3O_8 +$ degradation products

if there is a significant difference in the behaviour of $(UO_2Q_2)_2 \cdot HQ$ and of $UO_2Q_2 \cdot HQ$ which might suggest different modes of solvation of the molecule of 8-hydroxyquinoline.

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Zusammenfassung—Das thermogravimetrische Verhalten von

$UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ und $[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$

hergestellt durch Fällung aus homogener Lösung mit 8-Acetoxchinolin wurden als sehr ähnlich dem von $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ gefunden, welch letzteres durch direkte Fällung von Uran (VI) mit 8-Oxychinolin erhalten wurde.

Résumé—Les auteurs montrent que le comportement thermogravimétrique de

$UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ et de $[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$

préparés par précipitation au moyen de la 8-acétoxyquinoléine est très sensiblement le même que celui de $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ préparé par précipitation directe de l'uranium (VI) au moyen de la 8-hydroxyquinoléine.

REFERENCES

[1] C. Duval, *Inorganic Thermogravimetric Analysis.* Elsevier Publishing Co., New York 1953, p. 510.
[2] W. W. Wendlandt, *Analyt. Chem.*, 1956, **28**, 499.
[3] F. Hecht and W. Reigh-Rohrwig, *Monatsh.*, 1929, **53–54**, 596.
[4] J. Bordner, E. D. Salesin and L. Gordon, *Talanta*, 1961, **8**, 579.
[5] H. H. Willard and H. Diehl, *Advanced Quantitative Analysis.* D. Van Nostrand Co. Inc., Princeton, N.J., 1943, p. 80.

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NEW REDOX SYSTEMS—V*

OXIDATION OF URANIUM^{IV} WITH IRON^{III} IN 1,10-PHENANTHROLINE SOLUTIONS

INDIRECT COLORIMETRIC DETERMINATION OF URANIUM

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Summary—The oxidation of uranium^{IV} with iron^{III} in the presence of 1,10-phenanthroline has been studied both potentiometrically and colorimetrically. Suitable conditions for the indirect colorimetric determination of uranium via ferroïn have been found.

IN previous parts of this series the oxidation of cobalt^{II} with iron^{III} in the presence of 1,10-phenanthroline and 2,2-bipyridyl were reported.[1,2] It has now been found possible to oxidise uranium^{IV} quantitatively with iron^{III} under similar conditions. Because uranium^{IV} and uranium^{VI} form weak complexes with 1,10-phenanthroline or practically do not react at all and because the intensely coloured ferroïn results, the following course of reaction can be presumed:

$$U^{IV} + 2(Fe^{III})Phen \rightarrow U^{VI} + 2(Fe^{II})\,Phen \qquad (1)$$

The stoicheiometry of reaction (1) has been studied potentiometrically and especially colorimetrically. The obtained results have been utilised to develop a method for the indirect colorimetric determination of uranium^{IV}.

EXPERIMENTAL

Reagents

Standard uranium^{VI} solutions: Prepared from reagent grade $UO_2(NO_3)_2$ and their titre controlled gravimetrically as pyro-uranate. Before each test, suitable concentrations of uranium^{IV} were prepared by quantitative reduction of a standard uranium^{VI} solution with lead in 3*N* hydrochloric acid.[3]

Iron^{III} chloride solutions: Prepared from reagent grade $FeCl_3$ and their titre controlled gravimetrically as Fe_2O_3.

0·1*M* 1,10-*phenanthroline solution:* Prepared by dissolving 1·804 g of the analytically pure substance in water weakly acidified with sulphuric acid (resulting pH about 3) and diluting to 100 ml. Solutions of lower concentration were prepared by suitable dilution.

Buffer solutions: Prepared by neutralisation of the calculated quantity of trichloracetic, chloracetic or acetic acid with aqueous ammonia to the necessary pH, while a potentiometric control was maintained with a glass electrode. The resulting molarity of the solutions was 1.

Apparatus

The potentiometric measurements were carried out as previously.[1,2] The colorimetric measurements were carried out with a colorimeter Pulfrich with Elpho II (Carl Zeiss, Jena, E. Germany).

POTENTIOMETRIC RESULTS

In principle it is possible to oxidise uranium^{IV} in strongly acidic media with iron^{III} to uranium^{VI}. The comparatively high difference of standard potentials of the systems involved [$U^{IV}/U^{VI} = 0{\cdot}334$ V; $Fe^{II}/Fe^{III} = 0{\cdot}771$ V] allows the presumption of an

* Part IV: see reference 2.

easy quantitative oxidation. In practice, however, the oxidation of uranium^{IV} with iron^{III} only proceeds sufficiently quickly for analytical use at increased temperatures. Thus the results of the potentiometric determination of uranium show considerable errors. Better results can be obtained when potassium thiocyanate is used as a catalyst.[4] In the presence of 1,10-phenanthroline the oxidation of uranium^{IV} to uranium^{VI} with iron^{III} proceeds quantitatively at room temperature in the pH range 1·5–5 and the stabilisation of the potential is practically instantaneous.

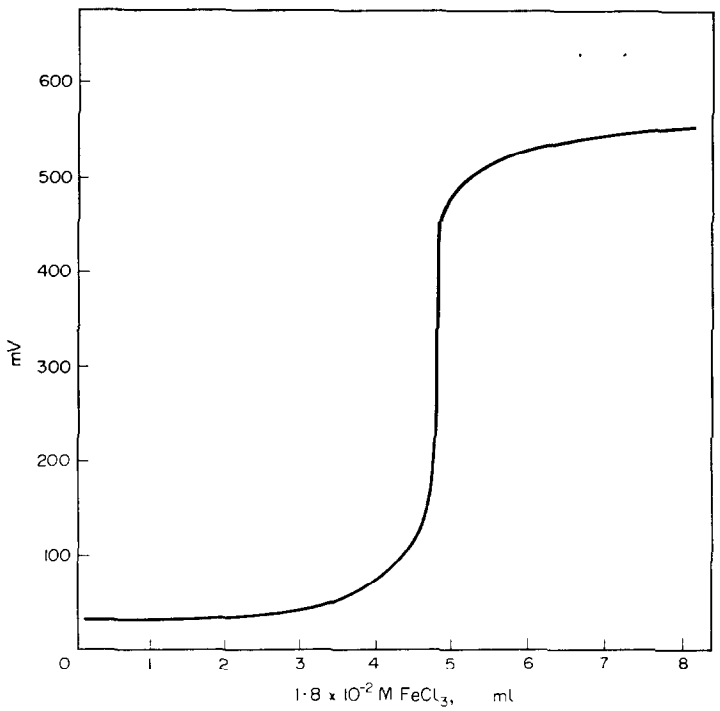


FIG. 1.—Oxidation of uranium^{IV} with iron^{III} chloride in 1,10-phenanthroline solution. (1 ml of $4{\cdot}5 \times 10^{-2}M$ uranium^{IV} solution; 5 ml of $0{\cdot}1M$ 1,10-phenanthroline solution; pH 2; total volume: 100 ml; titrated with $1{\cdot}8 \times 10^{-2}M$ iron^{III} chloride solution in an atmosphere of nitrogen, Pt-electrode *vs.* SCE.)

The reaction velocity is influenced by the presence of 1,10-phenanthroline, which might be explained by the binding of the iron^{II} formed during the reduction of iron^{III} with uranium^{IV} and by the increasing of the formal potential of the Fe^{II}/Fe^{III} system to the value 0·810 V at pH 2.[1]

Fig. 1 shows the course of a potentiometric titration curve of uranium^{IV} with iron^{III} in the presence of an excess of 1,10-phenanthroline in an atmosphere of nitrogen. The procedure was carried out as follows:

A given amount of uranium^{VI} solution was reduced with 5 g of granulated lead in $3N$ hydrochloric acid and 1,10-phenanthroline solution added. The solution was cautiously neutralised to pH 0·5–1, then adjusted to *ca.* pH 2 in an atmosphere of nitrogen, a buffer solution of the same pH added and finally titration carried out with iron^{III} chloride solution.

It is evident from the potentiometric curve that the oxidation of uranium^{IV} occurs quantitatively and quickly under the given conditions with a change of two electrons.

The calculated formal potentials of the studied systems show that the reaction occurs in accordance with the supposed course (1).

COLORIMETRIC RESULTS

Because of the intense red coloration of ferroïn developed during (1) (it is proportional to the uranium concentration), the reaction can be easily followed colorimetrically. The oxidation of uranium^{IV} with iron^{III} in the presence of 1,10-phenanthroline occurs considerably quicker than the oxidation of uranium^{IV} to uranium^{VI} with atmospheric oxygen and therefore it is not necessary to work in an inert atmosphere.

In the colorimetric study of reaction (1) the following procedure was used:

To the freshly prepared uranium^{IV} solution of pH < 1 a measured amount of iron^{III} chloride solution and 1,10-phenanthroline solution were added, and after adjustment of the pH to the chosen value, 5 ml of a suitable 1M buffer solution were added. The volume of the solution was adjusted to 25 ml and after 10 min the absorbance at 500–510 mμ was measured in a 5-cm cell against a blank solution prepared simultaneously with the sample and containing all of the reagents except the solution of uranium.

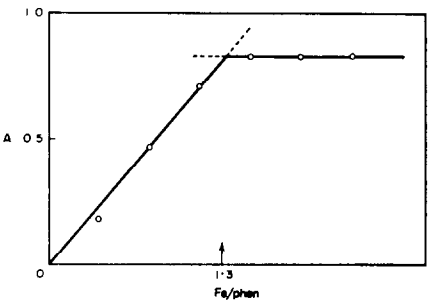


FIG. 2.—Dependence of the absorbance of $Fe(Phen)_3^{2+}$ resulting from the oxidation of uranium^{IV} with iron^{III} chloride solution on the ratio of uranium: iron. (1 ml of $4{\cdot}5 \times 10^{-4}M$ uranium^{IV} solution; 1 ml of 0·1M 1,10-phenanthroline solution; 2–10 ml of $1{\cdot}8 \times 10^{-4}M$ iron^{III} chloride solution; pH *ca.* 3; total volume: 25 ml; 5-cm cell; filter: $\lambda_{max} = 500$ mμ.)

Determination of the ratio of reacting components

The ratio of the reacting components was ascertained by the titration curve method. Fig. 2 shows that the quantitative oxidation of uranium in the presence of an excess of 1,10-phenanthroline requires a minimum ratio of uranium to iron of 1:2, which agrees with the results of the potentiometric titration. Fig. 3 shows the stoicheiometric amount of 1,10-phenanthroline necessary for the quantitative course of the reaction. The break in the curve at a ratio of iron:1,10-phenanthroline of 1:3 indicates that 1,10-phenanthroline is necessary only to bind the developed iron^{II} as the complex $Fe(Phen)_3^{2+}$.

From the results of the potentiometric and colorimetric studies and the fact that iron^{III} ions in a solution of pH 1·5–5 are bound with 1,10-phenanthroline as a hydroxo complex, the reaction can be described in detail by the equation:

$$U^{4+} + Fe_2(OH)_2(Phen)_4^{4+} + 2HPhen^+ \rightarrow UO_2^{2+} + 2Fe(Phen)_3^{2+} + 4H^+ \quad (2)$$

Influence of pH

The influence of pH on the ratio of reacting components of reaction (2) was also

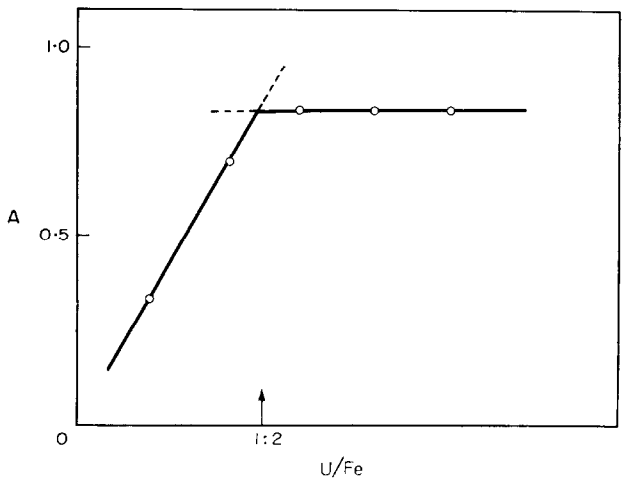


FIG. 3.—Dependence of the absorbance of $Fe(Phen)_3^{2+}$ resulting from the oxidation of uranium^{IV} with iron^{III} chloride solution on the ratio of iron: 1,10-phenanthroline. (1 ml of $4{\cdot}5 \times 10^{-4}M$ uranium^{IV} solution; 8 ml of $1{\cdot}8 \times 10^{-4}M$ iron^{III} chloride solution; 2–10 ml of $5 \times 10^{-4}M$ 1,10-phenanthroline solution; pH *ca.* 3; total volume: 25 ml; 5-cm cell; filter: $\lambda_{max} = 500$ mμ.)

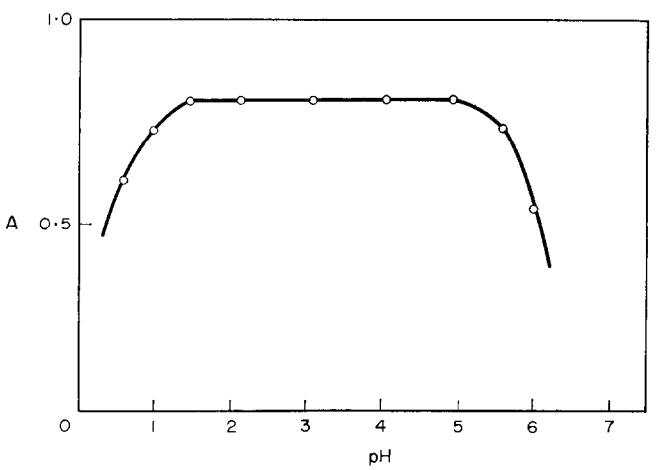


FIG. 4.—Dependence of the absorbance of $Fe(Phen)_3^{2+}$ resulting from the oxidation of uranium^{IV} with iron^{III} chloride solution on pH. (1 ml of $4{\cdot}5 \times 10^{-4}M$ uranium^{IV} solution; 3 ml of $0{\cdot}1M$ 1,10-phenanthroline solution; 8 ml of $1{\cdot}8 \times 10^{-4}M$ iron^{III} chloride solution; 5 ml of *ca.* $1M$ buffer solution; total volume: 25 ml; absorbance measured after 15 min; 5-cm cell; filter: $\lambda_{max} = 500$ mμ.)

followed colorimetrically. Fig. 4 shows that the oxidation of uranium^{IV} with iron^{III} in the presence of 1,10-phenanthroline proceeds quantitatively at pH 1·5–5.

Indirect colorimetric determination of uranium

The results obtained show suitable conditions for the indirect colorimetric determination of uranium via the formation of ferroïn during the oxidation of uranium^{IV} according to equation (2). It is only necessary to emphasise here the need for keeping a certain order in addition of the various reagents to eliminate the atmospheric oxidation of uranium^{IV}.

Procedure: To the solution of uranium^{VI} add sufficient hydrochloric acid to bring the normality to about 3. Pass the solution through a lead reductor of suitable size or shake it for some min with a suitable amount of granulated lead. After separation of the lead, adjust the pH cautiously and with constant stirring to 0·5–1, then add immediately 1 ml of 0·01*M* iron^{III} chloride solution and 1 ml of 0·1*M* 1,10-phenanthroline solution. Adjust the pH to about 2 and add 5 ml of 1*M* buffer solution of the same pH. After 10 min measure the absorption at 500–510 mμ against a blank solution prepared simultaneously with the sample and containing all of the reagents except the solution of uranium. The preparation of the sample solution simultaneously with the sample is necessary to compensate for the yellow coloration of $[Fe_2(OH)_2Phen_4]^{4+}$, formed by an excess of ions, and the optical density of which depends on time.[1]

Evaluation of the results is carried out with a calibration curve obtained from the values of the extinction of a series of standard uranium solutions processed in the same way as the sample. With 1-cm cells and a filter with maximum transmittance at 500–510 mμ the calibration curve is linear over the range of 0–0·45 mg of uranium/50 ml. The sensitivity of the method can be raised by using longer cells.

Interferences

Iron^{II} and cobalt^{II} are the main interferences with the proposed indirect colorimetric determination of uranium. Iron^{III}, after reduction with lead to iron^{II}, forms ferroïn with 1,10-phenanthroline and cobalt^{II} is oxidised by iron^{III} in the presence of 1,10-phenanthroline in the same way as uranium^{IV}. Similarly, tin^{II}, molybdenum^{III} and tungsten^{III} all cause high results in the indirect determination of uranium.

Ions, *e.g.* copper^{II}, zinc^{II}, nickel^{II}, which form relatively stable complexes with 1,10-phenanthroline also interfere with the determination because they bind the 1,10-phenanthroline necessary for the quantitative course of reaction (2). The unfavourable influence of these ions can be removed by the use of an excess of 1,10-phenanthroline. By using 1 ml of 0·1*M* 1,10-phenanthroline it is possible to determine 0·038 mg of uranium/50 ml in the presence of 10 mg of nickel, 3·5 mg of copper and 3·5 mg of zinc with an error of $\pm 2{\cdot}5\%$.

Some ions, *e.g.* bismuth^{III}, influence the indirect colorimetric determination of uranium as ferroïn because they are hydrolysed under the conditions, while others, *e.g.* cadmium^{II}, silver^{I}, mercury^{I}, perchlorate, form insoluble complexes with 1,10-phenanthroline. The influence of the latter can be removed by a sufficient excess of complex-forming reagent, but even then the resulting precipitates disturb the colorimetry of ferroïn. Alkali metals, calcium^{II}, magnesium^{II}, barium^{II}, rare earth elements, beryllium^{II}, lead^{II}, manganese^{II}, aluminium^{III}, gallium^{III}, indium^{III}, thorium^{IV} and zirconium^{IV} have no influence even at high concentrations. The same applies for high concentrations of sulphates, chlorides and nitrates. Some results are shown in Table I.

TABLE I.—INDIRECT COLORIMETRIC DETERMINATION OF URANIUM

Taken		Uranium found, μg	Error, % (*rel.*)
Uranium, μg	Other metal, *mg*		
9·50	—	9·61	+1·2
38·0	—	37·2	−2·1
104·0	—	101·0	−3·0
38·0	Ni 10	37·1	−2·1
38·0	Cu 3·5	38·5	+1·0
38·0	Zn 3·5	38·0	±0·0
38·0	Be 85·0	37·8	−0·5
38·0	Pb 107·5	38·8	+2·1
38·0	Th 62·5	37·5	−1·3

The proposed method is convenient for the determination of small concentrations of uranium after its separation especially from iron and cobalt. It can be applied reliably even if 5-cm cells are used for the determination of 10 μg of uranium/25 ml.

Zusammenfassung—Die Oxydation von Uran (IV) durch Fe (III) in Gegenwart von 1,10-Phenanthrolin wurde potentiometrisch und kolorimetrisch studiert. Die optimalen Bedingungen für eine indirekte Bestimmung von Uran via Ferroin wurden ermittelt.

Résumé—L'oxydation de U(IV) par Fe(III) en présence de 1,10-phénanthroline a été étudié par potentiométrie et par spectrophotométrie. Les conditions optimales du dosage colorimétrique indirect de l'uranium au moyen de la ferroïne ont été déterminées.

REFERENCES

[1] F. Vydra and R. Přibil, *Talanta*, 1959, **3**, 103; 1960, **5**, 44.
[2] *Idem, ibid.*, 1961, **8**, 824.
[3] R. Cooke, F. Hazel and W. N. McNabb, *Analyt. Chem.*, 1950, **22**, 654.
[4] J. Čihalík, *Potenciometrie*, ČSAV, Praha, 1961, p. 531.

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UNTERSUCHUNGEN AN REAGENZIEN FÜR NIOB UND TANTAL—I

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Zusammenfassung—Aus der Untersuchung einer großen Zahl hydroxylgruppenhaltiger organischer Substanzen konnten für weinsaure Lösungen als analytisch funktionelle Gruppierung für Niob und Tantal 2 Hydroxylgruppen in o-Stellung am aromatischen System erkannt werden. In gleicher Weise reagieren peri-Dihydroxynaphthalinderivate. Als Ergebnis der systematischen Untersuchungen wird Tribrompyrogallol als neues selektives und empfindliches Niobreagens gefunden.

BESTIMMUNG DER ANALYTISCH-FUNKTIONELLEN GRUPPE

Zu den noch keineswegs befriedigend gelösten Problemen der analytischen Chemie gehören auch die Methoden der Bestimmung von Niob und Tantal, besonders wenn diese beiden Elemente nebeneinander vorliegen.

Abgesehen von einigen anorgansichen Reagenzien werden meist Pyrogallol[2] und Brenzkatechin[3] für die Bestimmung der Erdsäuren benutzt, aber auch Phenylfluoron[4] u. a. werden in der Literatur empfohlen.

Auf der Suche nach geeigneten Reagenzien zur Bestimmung der Erdsäuren untersuchten Karjakin und Teleshnikowa[5] Phenole, Naphthole, Anthrachinonderivate u. a.. Als Komplexbildner benutzten sie Oxalat und Fluorid. Auf Grund ihrer Versuche empfahlen sie Pyrogallol, Brenzkatechin und Gallussäure zur Bestimmung der beiden Elemente.

Die nach dem Erscheinen der sowjetischen Arbeit beschriebenen neuen Reagenzien zeigten, daß eine nochmalige systematische Bearbeitung dieses Gebietes nützlich schien.

Im Rahmen dieser Untersuchung prüften wir sowohl aliphatische, wir aromatische Hydroxyverbindungen auf ihr Verhalten gegen Niob- und Tantal-Lösungen. Zur Beurteilung der Ergebnisse ist es noch von Bedeutung zu vermerken, daß die beiden Elemente als Tartratokomplexe eingesetzt wurden. Das Verhalten in oxalsaurer Lösung wurde zunächst nicht untersucht. Wegen der zu erwartenden pH-Abhängigkeit bei der Bildung der Komplexe führten wir die Untersuchungen sowohl im sauren, wie im neutralen und schwach alkalischen Gebiet durch.

Bei der Prüfung mit *weinsauren* Lösungen von Niob und Tantal ergaben

1. Mehrwertige aliphatische Alkohole (Glykol, Glyzerin, Mannit)	keine Reaktion
2. Einwertige Phenole und Derivate (Phenol, m-Kresol, Pikrinsäure)	keine Reaktion
3. Mehrwertige Phenole OH-Gruppen in m-Stellung (Phloroglucin, Resorcin, Orcin)	keine Reaktion

OH-Gruppen in p-Stellung (Hydrochinon)*	keine Reaktion
OH-Gruppen in o-Stellung (Brenzkatechin, Pyrogallol)	positive Reaktion
4. Einwertige Naphthole (α-Naphthol, β-Naphthol)	keine Reaktion
5. Mehrwertige Naphthole OH-Gruppen in m-Stellung (1.3-Dihydroxynaphthalin-5.7-disulfosäure)	keine Reaktion
OH-Gruppen in o-Stellung (2.3-Dihydroxynaphthalin)	positive Reaktion
OH-Gruppen in peri-Stellung (Chromotropsäure)	positive Reaktion
6. Dihydroxyanthracenderivate OH-Gruppen in o-Stellung (Alizarin, Chinalizarin)	positive Reaktion

Aus diesen Untersuchungen geht hervor, daß man o-ständige OH-Gruppen an aromatischen Ringen als analytisch- funktionelle Gruppen ansehen muß.

In einer weiteren Versuchsreihe prüften wir Substanzen, bei denen eine der Hydroxylgruppen durch Carboxyl-, Aldehyd- bzw. Methoxylgruppe ersetzt war. Bei keiner der Substanzen konnte in Gegenwart von Weinsäure eine Reaktion mit den Erdsäuren festgestellt werden.

Das Verhalten des Toluol-3.4-dithiols zeigte jedoch, daß o-ständige Sulfhydrylgruppen ähnlich wirken wie OH-Gruppen.

AUSWAHL GEEIGNETER REAGENZIEN

Zur Bestätigung des Ergebnisses der im ersten Abschnitt beschriebenen Versuche untersuchten wir im Anschluß daran eine größere Anzahl von Substanzen, die o-ständige Hydroxylgruppen enthalten mit dem Ziel, dabei geeignete Verbindungen für die photometrische Bestimmung zu finden.

Die Prüfung der Lösungen erfolgte durch photographische Aufnahme der Absorptionsspektren im Gebiet von ca. 350 bis 650 nm. Zur besseren Auswertung wurden die mittels Registrierphotometer erhaltenen Schwärzungskurven der Photoplatten herangezogen.

Da alle geprüften Reagenzien mit den Erdsäuren gelbe bis rote Verbindungen ergaben, sollen im folgenden nur die untersuchten Verbindungen aufgezählt werden, ohne daß zunächst auf die Absorptionsspektren eingegangen wird.

Wir prüften: Andrenalin, Alizarin, Brenzkatechin, Brenzkatechinviolett, Brompyrogallolrot, Carminsäure, Chinalizarin, Chromotropsäure, 2.3-Dihydroxynaphthalin, Dithiol, Gallussäure, Hämatoxylin, Phenylfluoron, Pyrogallol, Quercetin, Tiron, Tribrompyrogallol.

Für die weiteren Untersuchungen wählten wir aus diesem Sortiment die Stoffe aus, bei denen sich die Spektren der Metallkomplexe möglichst stark von denen der reinen

* Das bekannte Verfahren zur Bestimmung von Niob in stark schwefelsaurer Lösung[6] beruht sicher auf einer Redox-Reaktion, kann also hier außer acht gelassen werden.

Reagenzien unterscheiden. Die Verhältnisse liegen natürlich besonders günstig, wenn die Reagenzlösungen farblos sind.

Unter diesen Gesichtspunkten erwiesen sich als besonders geeignet: Brenzkatechin, Chromotropsäure, Pyrogallol und Tiron.

Da—wie allgemein bekannt ist—die Einführung von Halogenatomen in organische Moleküle eine Farbvertiefung ergibt, untersuchten wir in diesem Zusammenhang das präparativ leicht zugängliche Tribrompyrogallol. Tetrabrombrenzkatechin, das ebenfalls leicht darstellbar ist, zeigt schlechte Löslichkeit und scheidet deshalb für analytische Zwecke aus. Die Untersuchung des Tribrompyrogallols ergab die erwarteten Effekte, so daß es mit in die Reihe der empfehlenswerten Reagenzien aufgenommen wurde.

AUFNAHME DER ABSORPTIONSSPEKTREN

Da zu erwarten war, daß die Färbung der Komplexe vom pH-Wert der Lösung abhängig ist, für die folgenden Untersuchungen aber die Bedingungen gefunden werden sollten, bei denen die Spektren im Sichtbaren eine maximale Farbintensität zeigen, prüften wir zunächst den Einfluß der Wasserstoffionenkonzentration.

Die Ergebnisse sind in Abb. 1 graphisch dargestellt.

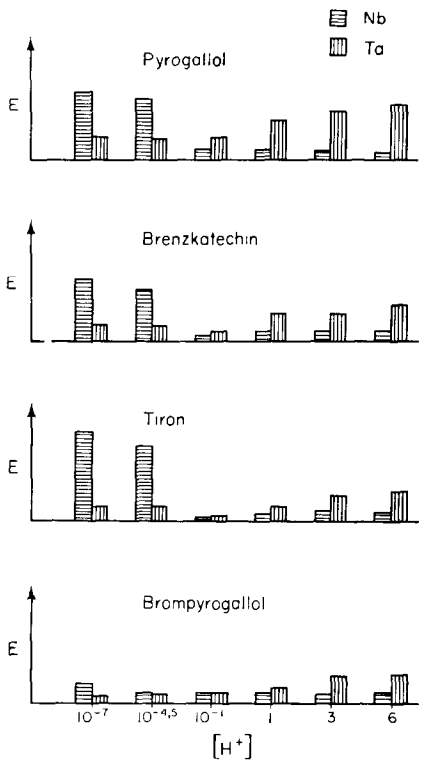


ABB. 1.—Absorption der Niob- und Tantalkomplexe bei $\lambda = 400$ nm in Abhängigkeit von der Wasserstoffionenkonzentration.

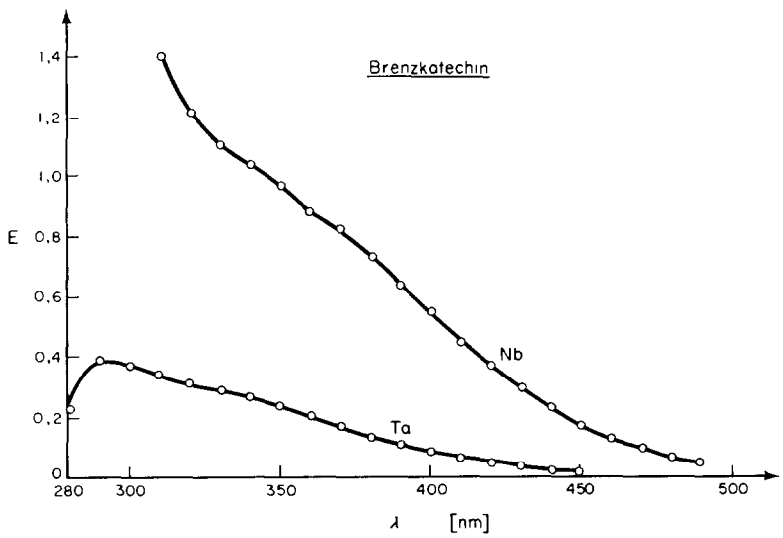
Das Schema, das nur einen qualitativen Vergleich zuläßt, zeigt, daß bei allen Reagenzien die Niob-Komplexe in neutraler, die Tantalkomplexe in stark saurer Lösung die intensivste Färbung aufweisen.

Im Zusammenhang mit diesen Versuchen stellten wir außerdem noch fest, daß die Färbungen nach spätestens 30 min ihr Maximum erreichen und dann für längere Zeit konstant bleiben. Zur Verhinderung der Oxydation des Pyrogallols mußte bei den Messungen im neutralen Gebiet den Lösungen etwas Natriumsulfit zugesetzt werden.

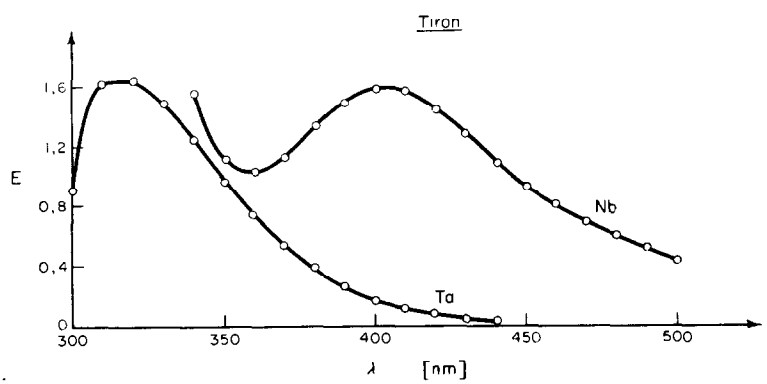
Bei dieser und allen weiteren Untersuchungen befanden sich im Vergleichsstrahlengang die reinen Reagenzlösungen der entsprechenden Wasserstoffionenkonzentration um deren Eigenabsorption im ultravioletten Spektralbereich auszuschalten.

Anschließend nahmen wir dann die Absorptionsspektren bei der Wasserstoffionenkonzentration auf, bei der wir vorher die höchste Extinktion gemessen hatten (Nb im Neutralen, Ta in 6*M* HCl).

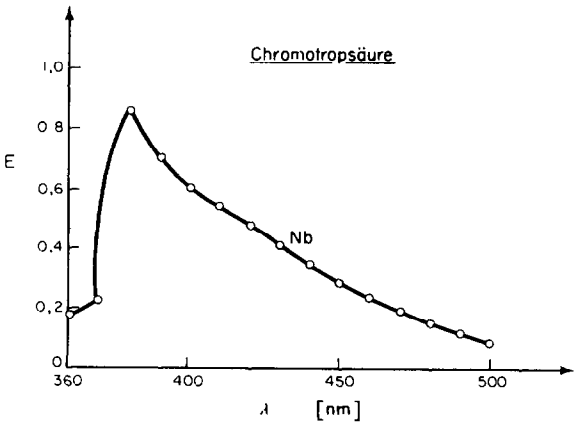
Die Konzentration der Metallionen wählten wir dazu so, daß im Gebiet maximaler Extinktion gut meßbare Werte erhalten werden konnten. Die so erhaltenen Spektren sind in den Abb. 2a–e wiedergegeben.



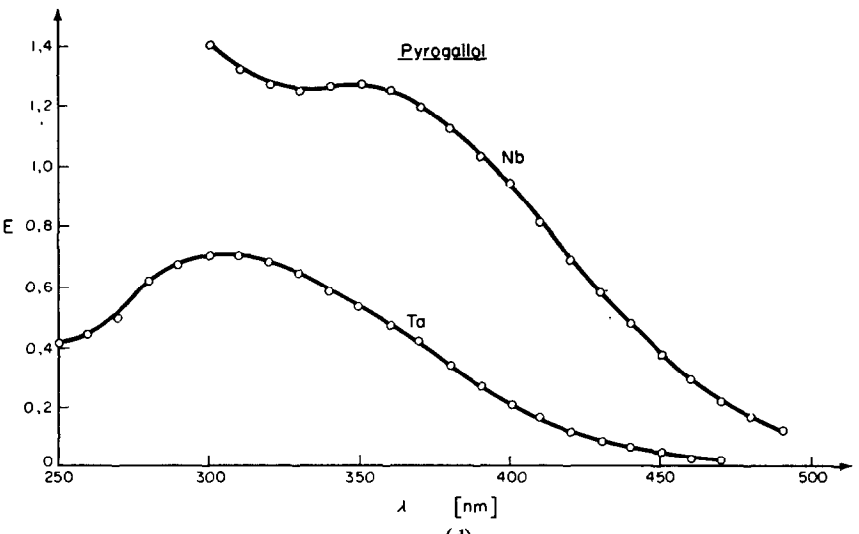
(a)



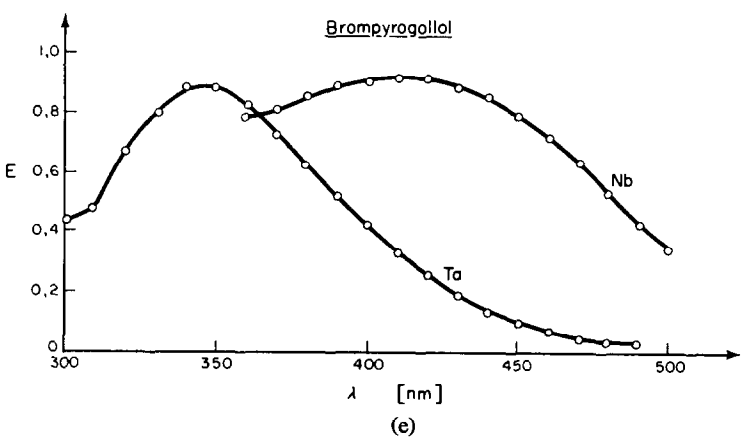
(b)



(c)



(d)



(e)

ABB. 2a–e.—Absorptionsspektren der Niob- und Tantalkomplexe.

In Tabelle I sind die Wellenlängen der Maxima der Spektren der Niob- und Tantalkomplexe zusammengestellt.

TABELLE I.—LAGE DER MAXIMA DER ABSORPTIONSSPEKTREN DER NIOB- UND TANTALKOMPLEXE

Reagens	Niob λ_{max}, *nm*	Tantal λ_{max}, *nm*
Brenzkatechin	350	295
Tiron	405	320
Chromotropsäure	380	
Pyrogallol	350	310
Tribrompyrogallol	410	345

Aus der Tabelle läßt sich ablesen, daß die Absorptionsmaxima der Tantalkomplexe stets bei kleineren Wellenlängen liegen als die der Niobverbindungen.

Für die Anwendung der Reagenzien sollen die Maxima der Nb- und Ta-Spektren möglichst weit auseinander liegen. In dieser Hinsicht ist das Tiron am günstigsten. Man kann aber erkennen, daß auch beim Tribrompyrogallol die Verhältnisse recht günstig liegen. Durch die Bromierung ist der Abstand der Maxima der beiden Spektren größer geworden (Nb von 350 auf 410 mm; Ta von 310 auf 345 nm).

In Tabelle II sind die Maximalkonzentrationen zusammengestellt bis zu welchen das Beersche Gesetz durch die untersuchten Erdsäurekomplexe erfüllt wird.

TABELLE II.—MAXIMALE KONZENTRATIONEN BIS ZU WELCHEN DAS BEERSCHE GESETZ ERFÜLLT WIRD

Reagens	Niob, *µg/ml*	Tantal, *µg/ml*
Brenzkatechin	100	2200
Tiron	60	250
Chromotropsäure	140	
Pyrogallol	50	1000
Tribrompyrogallol	30	2100

Ein quantitativer Vergleich der Brauchbarkeit der Reagenzien läßt sich am besten an Hand der molaren Extinktionskoeffizienten anstellen, die in Tabelle III enshalsen sind.

TABELLE III.—MOLARE DEKADISCHE EXTINKTIONSKOEFFIZIENTEN DER NIOB- UND TANTALKOMPLEXE MIT POLYPHENOLEN UND DERIVATEN DAVON

Reagens	neutral			sauer		
	λ, *nm*	Nb	Ta	λ, *nm*	Nb	Ta
Brenzkatechin	350	2640	227	295	801	143
Tiron	405	5060	93	320	641	1070
Chromotropsäure	380	1348	356			
Pyrogallol	350	5630	326	310	563	337
Tribrompyrogallol	410	6170	11	345	107	267

Um den Umfang der Störung der Meßwerte des einen Elementes durch das andere beurteilen zu können, sind auch die Extinktionskoeffizienten für Niob unter den für Tantal optimalen Bedingungen und umgekehrt bestimmt worden. Die Übersicht

zeigt deutlich, daß unter den geprüften Reagenzien der Niob-Brompyrogallolkomplex den höchsten Extinktionskoeffizienten aufweist und hier die Störung durch Tantal außerordentlich gering ist.

Auf Grund dieser Befunde kann Tribrompyrogallol als neues Reagens für die photometrische Bestimmung von Niob empfohlen werden.

Andererseits ist zu erkennen, daß alle untersuchten Reagenzien sich in weinsaurem Medium nicht besonders gut zur Bestimmung des Tantals eignen, wobei das Tiron noch die günstigsten Ergebnisse zeigt. Auf Grund der Tatsache, daß im Tribrompyrogallol ein weitgehend selektives Reagens vorliegt, kann für die Simultanbestimmung von Niob und Tantal in weinsaurer Lösung folgendes Verfahren empfohlen werden.

1. Bestimmung des Niobs in neutraler Lösung bei 410 nm unter Verwendung von Tribrompyrogallol.

2. Bestimmung der Summe Niob + Tantal in 6*M* salzsaurer Lösung mit Tiron bei 320 nm.

3. Ermittlung der Extinktion des Niob-Tiron-Komplexes unter den Bedingungen von 2. aus einer gesondert aufgenommemen Störkurve.

4. Errechnung des Ta-Gehaltes aus der Differenz (Σ Nb + Ta) (bestimmt nach 2.) und dem Niobgehalt (bestimmt nach 1).

EXPERIMENTELLER TEIL

Apparaturen

Die spektrophotometrischen Messungen erfolen mit dem Universalspektrophotometer VSU 1 des VEB Carl Zeiss, Jena.

Herstellung der Lösungen der Erdsäuren

1. *Niob-Testlösung:* 3,3219 g des nach Brauer[7] gereinigten Niob(V)-oxids werden mit 30 g Kaliumhydrogensulfat im Quarztiegel aufgeschlossen und in 150 ml Weinsäurelösung (200 g/l) unter Erwärmen gelöst. Darauf Auffülen mit Wasser auf 250 ml. Die so erhaltene Lösung ist 0,1*M* an Niob. 1 ml = 9,3 mg Niob.

2. *Tantal-Testlösung:* 5,5234 g reinstes Tantal(V)-oxid werden mit 70 g Kaliumhydrogensulfat zwei Stunden im Quarztiegel geschmolzen. Zum Ende des Aufschlusses muß der Verlust an Schwefeltrioxid durch Zugabe einiger Tropfen konzentrierter Schwefelsäure ausgeglichen werden. Die erkaltete Schmelze wird mit 250 ml Weinsäurelösung (200 g/l) etwa 5 min zum Sieden erhitzt, abgekühlt und im Meßkolben auf 250 ml aufgefüllt. Die so erhaltene Lösung ist 0,1*M* an Tantal. 1 ml = 18,1 mg Tantal.

3. *Tribrompyrogallol:* Die Herstellung des Reagenses erfolgte nach einer Vorschrift von Hlasiwetz.[8]

12,6 g Pyrogallol wurden mit 50 g Brom in einer Reibschale verrieben und das nicht verbrauchte Brom auf dem siedenen Wasserbad abgedampft. Das Rohprodukt wurde aus siedendem Wasser umkristallisiert und getrocknet.

Schmelzpunkt: nach Literatur 168–170°; gefunden 170°.

4. *Reagenzlösungen*

Brenzkatechin	20%ig in Wasser
Pyrogallol	20%ig in Wasser
Tiron	20%ig in Wasser
Chromotropsäure	1%ig in Wasser
Tribrompyrogallol	10%ig in Äthanol

Summary—On examination of a wide range of hydroxylic organic compounds it has been found that two hydroxyl groups in the *ortho* position to each other in an aromatic system act as a functional analytical group for niobium and tantalum. *peri*-Dihydroxynaphthalene derivatives react similarly. After a systematic examination, tribromopyrogallol is proposed as a new selective and sensitive reagent for niobium.

Résumé—Au cours de l'étude d'un grand nombre de composés organiques oxhydrilés, il a été constaté qu'en présence d'acide tartrique, les composés possédant deux groupements oxhydriles en ortho sur un noyau aromatique présentaient des propriétés analytiques spécifiques pour le niobium et le tantale. Les dérivés du péri-dihydroxynaphtalène réagissent d'une manière analogue. Après une étude systématique, le tribromopyrogallol est proposé comme un nouveau réactif spécifique et sensible du niobium.

LITERATUR

[1] S. Koch, Diplomarbeit Freiberg, 1961.
[2] A. E. O. Marzys, *Analyst*, 1955, **80**, 194.
[3] O. Tomiček u. L. German, *Chem. Listy*, 1952, **46**, 144.
[4] P. Senise u. L. Sant'Agostino, *Analyt. Chim. Acta*, 1960, **22**, 296.
[5] J. W. Karajakin u. P. M. Teleshnikowa, *Zhur. priklad. Khim.*, 1946, **19**, 435.
[6] L. Ikenberry, J. L. Martin u. W. I. Boyer, *Analyt. Chem.*, 1953, **25**, 1340.
[7] G. Brauer, *Handbuch der präparativen anorganische Chemie*, Stuttgart, 1954.
[8] H. Hlasiwetz, *Annalen*, 1867, **142**, 250.

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DETERMINATION OF METALS IN METAL CHELATE COMPOUNDS*

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Summary—A rapid and convenient method of determining the metal content of metal chelate compounds is reported. The sample is decomposed with mixed acids in an open tube, and the freed metal ion is titrated with EDTA. Of the mixed acids investigated, a 3:1 mixture of nitric acid (62%) and perchloric acid (60%) is found to be effective in most cases.

THE determination of the metal content of solid metal chelate compounds has been done in various ways. The classical method of dry ashing, with or without sulphuric acid, cannot be recommended as the standard procedure, since there is a danger of sublimation of sample. There remains the further problem of choosing the weighing forms, metal oxide or sulphate, if the determination is finished gravimetrically.

Since the development of EDTA titration techniques for the determination of metals, many papers have been published on the application of this method to the determination of metals in chelate compounds. In these methods, the samples are at first decomposed by wet-digestion processes. Once the ligand molecule is decomposed and the free metal ion is released into solution, the subsequent metal titration can be done without difficulty.[1,2] In order to decompose the metal chelates without loss of sample, various procedures have been proposed. For example, samples may be decomposed by a modified Kjeldahl digestion method, by fuming nitric acid in an open or a sealed tube, or by the Schöniger flask combustion method.[3–5] Most of the chelates which are difficult to decompose can be degraded satisfactorily either by the Kjeldahl method or by modified Carius method with fuming nitric acid in a sealed tube.[6] However, in the case of the Kjeldahl method, excess sulphuric acid often causes trouble in the subsequent metal titration; and the Carius decomposition is time-consuming. Decomposition of the sample with fuming nitric acid in an open vessel often results in a violent spontaneous combustion which causes splashing of the sample. The Schöniger method seems attractive in its simplicity, but the method is only applicable to chelates of the alkaline earths, zinc, cadmium or mercury, because other metals form alloys with the platinum wire, or form insoluble oxides.[3]

The present investigation was carried out to find the most practical method of determining the metal content of chelate compounds. For the sake of simplicity in the analytical procedure, the methods investigated are all wet-digestion processes in open vessels. Of these, the following digestion procedures are found to give satisfactory results: (1) with fuming or concentrated nitric acid, (2) with a mixture of concentrated nitric acid and concentrated sulphuric acid, (3) with a mixture of concentrated

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nitric acid and perchloric acid, and (4) with a mixture of fuming nitric acid, concentrated sulphuric acid and perchloric acid.

Although the last of these procedures offers the most complete and smooth decomposition, it has a drawback in that insoluble sulphate may result from barium and lead chelates. Procedures (1) and (2), if carried out carefully, also provided satisfactory results for most of the metal chelates investigated. Procedure (3), employing a mixture of nitric acid and perchloric acid, was found to be the most useful for a wide variety of samples.

Although these procedures were originally developed for the determination of metals in metal chelate compounds, they may also be useful for such samples as the metal salts of organic acids or other organometallic compounds.

EXPERIMENTAL

Reagents

Decomposition mixtures

(1) Fuming nitric acid.
(2) A mixture of 15 ml of nitric acid (62%) and 15 ml of hydrogen peroxide (30%).
(3) A mixture of 15 ml of nitric acid (62%) and 15 ml of sulphuric acid (95%).
(4) A mixture of 18 ml of nitric acid (62%) and 6 ml of perchloric acid (60%).
(5) A mixture of 15 ml of fuming nitric acid, 15 ml of sulphuric acid (95%) and 5 ml of perchloric acid (60%).

Reagents for EDTA titration

0·005M *EDTA solution*: Dissolve about 1·86 g of disodium ethylenediaminetetraacetate dihydrate in distilled water to make 1 litre, and standardise against 0·01*M* standard zinc sulphate solution at pH 10 using Erio T as indicator.

Metallochromic indicators: Erio T, Patton and Reeder's Dye, Xylenol Orange, and Pyridylazonaphthol (PAN). Conditions for the metal titrations are listed in Table I. Sodium was determined on an aliquot of the decomposed solution, by precipitation as sodium zinc uranyl acetate, followed by the EDTA titration of zinc in the precipitate.[7,8]

Other reagents

Analytical grade unless otherwise stated. Demineralised water is used throughout the experiments.

Procedure

Weigh about 10–20 mg of sample into a small test tube (10 mm in diameter and 12 cm in length). To this, add 10 drops of decomposing acid drop by drop. Care should be taken not to leave any sample on the wall of the tube, otherwise it will be incompletely decomposed, or will be lost by

TABLE I.—CONDITIONS FOR THE METAL TITRATIONS

Metal ion	Indicator	Buffer and pH
Mg	Erio T	NH_3—NH_4Cl, 10
Ca	Patton and Reeder	KOH 13
Sr	Erio T, Mg-EDTA	NH_3—NH_4Cl, 10
Ba	Erio T, Mg-EDTA	NH_3—NH_4Cl, 10
Zn	Erio T	NH_3—NH_4Cl, 10
Cd	Erio T	NH_3—NH_4Cl, 10
Hg^{II}	Xylenol Orange	Urotropin, 6
Cu	PAN	Acetate, methanol, 2·5
Ni	PAN, Cu-EDTA	Acetate, 3, (100°)
Pb	Xylenol Orange	Urotropin, 6
	Erio T (Back titration with Zn)	NH_3—NH_4Cl, 10
Bi	Xylenol Orange	HNO_3, 1–3

sublimation during the decomposition process. Hold the tube at a 45° angle, and heat very carefully at the bottom by a microburner. Shake the tube continually to avoid explosive boiling. At the first stage of decomposition, evolution of nitrogen oxides is observed, then fuming of sulphuric acid or perchloric acid follows. Continue heating for about 5–10 min until only a few drops of the liquid remain in the tube.

After cooling, wash the content of the tube into a titration flask, and dilute for the metal titration. The conditions of titration for each metal are summarised in Table I.

If the sample contains a relatively large ligand or one difficult to decompose, it is sometimes necessary to repeat the decomposition with a few additional drops of the acid.

RESULTS AND DISCUSSION

The relative ease of sample decomposition depends greatly on the kind of metal chelates investigated, and some examples of metal determinations are listed in Table II–IV.

Simple chelate compounds can be decomposed by nitric acid if heating is applied slowly. If the sample is heated in a wide open vessel such as a crucible or beaker, in place of a narrow tube, loss of sample occurs during the violent spontaneous decomposition reaction, which often occurs at a later stage in the decomposition process.

In the case of nitrilotriacetate chelates, the sample can be decomposed satisfactorily by a mixture of nitric acid and hydrogen peroxide, but not by nitric acid only. As shown in the examples, the sodium content can also be determined on an aliquot of the resulting solution. Determination of the metal content of such metal chelates cannot be achieved by the classical gravimetric methods after dry ashing.

TABLE II.—METAL DETERMINATION AFTER DECOMPOSING WITH FUMING NITRIC ACID

Sample	Metal, %	
	Calcd.	Found.*
$Bi(NH_2CH_2CH_2S)_2(NO_3)$	49·37	49·3
$Ni(NH_2CH_2CH_2S)(OH_2)_3(NO_3)$	23·40	23·6
$Ni(NH_2CH_2CH_2S)_2$	26·96	26·8
$Pb(NH_2CH_2CH_2S)(OH_2)_5NO_3)$	45·74	46·0
$Hg(NH_2CH_2CH_2S)(OH_2)_2(NO_3)$	53·51	53·8

* The values reported in Table II–IV are the average of two to five determinations.

TABLE III.—METAL DETERMINATION AFTER DECOMPOSING WITH A MIXTURE OF NITRIC ACID AND HYDROGEN PEROXIDE

Sample	Metal, %		Na, %	
	Calcd.	Found	Calcd.	Found
NaMgNTA* ·$3.5H_2O$	8·16	8·10	7·72	7·68
NaCaNTA·$3H_2O$	14·02	14·02	7·54	7·50
NaSrNTA·$4H_2O$	23·5	24·0	6·22	6·12
NaBaNTA·$3·5H_2O$	33·4	34·0	5·59	5·50
NaNiNTA·$3·5H_2O$	17·6	17·0	6·91	6·68
NaCuNTA·$2·5H_2O$	19·9	20·6	7·22	7·06
NaZnNTA·$3·5H_2O$	19·3	19·4	6·67	6·60
NaCdNTA·$3H_2O$	30·3	31·0	6·15	6·08
NaPbNTA·$3H_2O$	43·9	44·2	4·87	4·80

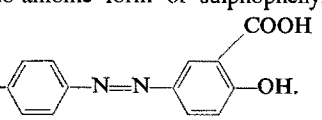
* NTA designates trivalent anionic form of nitrilotriacetic acid, $N(CH_2COO)_3^{-3}$.

In most cases, a mixture of nitric acid and perchloric acid is found to be a most effective oxidising agent, reacting smoothly. No violent reaction is observed with a mixture containing perchloric acid or sulphuric acid, but the mixture containing sulphuric acid gives insoluble precipitates in the case of lead and barium chelates. However, this is not a serious defect since those precipitates can be dissolved in alkaline EDTA solution, making it possible to determine them by a back-titration technique.

TABLE IV.—METAL DETERMINATION AFTER DECOMPOSING WITH NITRIC ACID, OR WITH MIXTURES WITH SULPHURIC ACID OR PERCHLORIC ACID

Sample	Decomposing acid.*	Metal, %	
		Calcd.	Found
Bis(acetylacetonato)-Cu^{II}	(1)	24·27	24·1
Bis(acetylacetone)-ethylenedi-imino-Cu^{II}	(1)	22·23	22·0
	(3)	22·23	22·2
Bis(salicylaldi-imine)-diethylenesulphido-Cu^{II}	(1)	16·30	15·6
	(4)	16·30	15·5
$Mg(SAS)_2.8H_2O$†	(4)	3·00	3·01

* Number of acid stands for the number of the decomposition mixture as listed under Reagents.

† SAS designates a mono-anionic form of sulphophenylazo-salicylic acid, $^{-}O_3S$—  —OH.

In some instances, such as metal chelates of sulphophenylazosalicylic acid, decomposition with the mixture of nitric acid and perchloric acid is not complete and it is necessary to repeat the digestion with an additional amount of acid.

Zusammenfassung—Eine schnelle und einfache Methode zur Bestimmung des Metallgehaltes von Chelatverbindungen wird mitgeteilt. Die Probe wird im offenen Rohr mit einem Säuregemisch zersetzt und das Metall mit ADTE titriert. Von den untersuchten Säuremischungen wurde die folgende als sehr wirkungsvoll gefunden: 3 Teile (62%) Salpeter—und 1 Teil (60%) Perchlorsäure.

Résumé—Les auteurs proposent une méthode rapide et commode pour le dosage d'un métal contenu dans un complexe. L'échantillon est décomposé par un mélange d'acides en tube ouvert, et le métal, libéré, est titré par l'E.D.T.A. Parmi les mélanges d'acides étudiés, le mélange de 3 parties d'acide nitrique (62%) et d'une partie d'acide perchlorique (60%) s'est révélé le plus efficace dans la majorité des cas.

REFERENCES

[1] G. Schwarzenbach, *Die Komplexometrische Titration*, Ferdinand Enke, Stuttgart, 1956.
[2] K. Ueno, *Chelatometric Titration*, Nankodo, Tokyo, 1960.
[3] R. Belcher, A. M. G. Macdonald and T. S. West, *Talanta*, 1958, **1**, 408.
[4] B. C. Southworth, J. H. Hodecker and K. D. Fleischer, *Analyt. Chem.*, 1958, **30**, 1152.
[5] J. E. Barney, II, J. G. Bergmann and W. G. Tuskan, *ibid.*, 1959, **31**, 1394.
[6] P. J. McCarthy, R. J. Hovey, K. Ueno and A. E. Martell, *J. Amer. Chem. Soc.*, 1955, **77**, 5820.
[7] H. Flaschka, *Mikrochem. Mikrochim. Acta*, 1952, **39**, 38.
[8] B. Sen, *Z. analyt. Chem.*, 1957, **157**, 2.

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EXTRACTION AND DETERMINATION OF IRON AS THE BATHOPHENANTHROLINE COMPLEX IN HIGH-PURITY NIOBIUM, TANTALUM, MOLYBDENUM AND TUNGSTEN METALS*

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Summary—A spectrophotometric method for determining iron in the range 0·001–0·125% in high-purity niobium, tantalum, molybdenum and tungsten metals is described. After sample dissolution and reduction of iron to the bivalent state with ascorbic acid and hydroxylamine hydrochloride, the red complex formed between iron^{II} and bathophenanthroline (4,7-diphenyl-1,10-phenanthroline) is extracted into *n*-amyl alcohol and the absorbance of the resulting extract is determined at 536 mμ. Interference from copper is eliminated with thiourea. Cobalt, cadmium, nickel, manganese and zinc also interfere but the amounts of each of these impurities present in the four high-purity metals described are so low that their interference effects are negligible in the proposed method. Highly reproducible and precise results can be obtained with careful control of the pH during reduction and extraction.

INTRODUCTION

THE development of a suitable spectrophotometric procedure for the determination of trace amounts of iron in high-purity niobium, tantalum, molybdenum and tungsten metals has been undertaken at the Mines Branch laboratories as part of a project to determine impurities in these metals.

Despite the large number of spectrophotometric methods which have been proposed for the determination of small amounts of iron, very few have been applied in matrices of the above metals. Hastings *et al.*[1] determined iron in tantalum metal with *o*-phenanthroline. Crawley and Aspinal[2] used bathophenanthroline for the determination of iron in tungsten metal. Recently Gahler *et al.*[3] described a method for determining iron in niobium, tantalum and tungsten metals with bathophenanthroline in which iron is reduced with sodium dithionite and the iron^{II}-bathophenanthroline complex is extracted into chloroform. Their procedure could probably be extended to the determination of iron in molybdenum metal but this was not attempted because the present investigation was nearing completion at the time their paper was published. Prior to this time no single method was found in the literature which was directly applicable to all four metals under consideration.

At the beginning of this investigation it was decided that the development of a single procedure applicable to all four metals would require similar methods of dissolution and solution preparation, as well as a chromogenic reagent capable of forming an extractable iron complex. The use of an extraction procedure would be necessary

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to remove the coloured iron complex from the background colour exhibited by molybdenum solutions and also possible turbidity from partial hydrolysis of niobium and tantalum solutions. The extraction step would increase the sensitivity of the method and also make it possible to remove iron from solutions of the required agents, thus reducing the blank essentially to zero.

It is known that the four high-purity metals dissolve in hydrofluoric and nitric acids and form soluble complexes with ammonium tartrate.[2,4,5] Therefore, these reactions were utilised for the decomposition procedure and solution preparation. Bathophenanthroline was chosen as the chromogenic reagent because of its sensitivity and reported specificity.[6] It was first proposed by Case,[7] and investigated as an analytical reagent by Smith, McCurdy and Diehl[8] who applied it to the determination of iron in municipal water supples. The iron^{II}-trisbathophenanthroline complex has a molar extinction coefficient of 22,400 at 533 mμ[8] and can be extracted into iso-amyl, *n*-amyl and *n*-hexyl alcohols, and nitrobenzene.[6]

The present paper describes the successful use of bathophenanthroline in determining iron in high-purity niobium, tantalum, molybdenum and tungsten metals. Copper, cobalt, cadmium, nickel, manganese and zinc were found to interfere in this method. In the aliquot taken for analysis up to 10 μg of each of these interfering cations can be tolerated, while the tolerance level for copper alone is 50 μg.

EXPERIMENTAL

Apparatus

Spectrophotometer: Beckman Model DU.
pH meter: Leeds and Northrup, Cat. No. 7664, a.c. operated.
Centrifuge: Canlab clinical type.

Reagents

Standard iron stock solution: Dissolve 0·1000 g of electrolytic iron in 10 ml of 1:1 sulphuric acid. Dilute to 500 ml with water and store in a polyethylene bottle.

Pre-reduced standard iron solution: Dilute 5 ml of the stock solution together with 1 ml of 10% ascorbic acid solution to 200 ml with water. Prepare fresh as needed (1 ml of this solution ≡ 5 μg Fe).

Bathophenanthroline, 0·001M solution: Dissolve 0·167 g of 4,7-diphenyl-1,10-phenanthroline (G. Frederick Smith Chemical Co.) in 250 ml of ethyl alcohol. Dilute to 500 ml with water and store in a polyethylene bottle.

Ammonium tartrate, 25% iron-free solution: Dissolve 125 g of ammonium tartrate and 1 g of hydroxylamine hydrochloride in approximately 350 ml of water. Add 10 ml of bathophenanthroline solution, allow to stand for 1 hr, then extract three times with 15-ml portions of a 3:1 mixture of chloroform and *n*-amyl alcohol. Extract the iron-free solution three times with chloroform to remove excess *n*-amyl alcohol. Filter, dilute to 500 ml with water and store in a polyethylene bottle.

Boric acid, 5% iron-free solution: Dissolve 50 g of boric acid in approximately 800 ml of hot water. Cool, dissolve 1 g of hydroxylamine hydrochloride in this solution, then add 20 ml of bathophenanthroline solution and allow to stand for 1 hr. Extract with chloroform and *n*-amyl alcohol as described for the ammonium tartrate solution. Filter, dilute to 1 litre with water and store in a polyethylene bottle.

Hydroxylamine hydrochloride, 10% iron-free solution: Dissolve 10 g of hydroxylamine hydrochloride in approximately 60 ml of water. Add 5 ml of bathophenanthroline solution and allow to stand for 10 min. Extract three times with 8-ml portions of a 3:1 mixture of chloroform and *n*-amyl alcohol, then three times with chloroform to remove excess *n*-amyl alcohol. Filter and dilute to 100 ml with water. Prepare a fresh solution weekly.

Ascorbic acid, 10% solution: Dissolve 10 g of ascorbic acid (Analytical Reagent, British Drug Houses Ltd.) in water and dilute to 100 ml. Prepare a fresh solution every second day. (The iron content of this reagent is sufficiently low that purification is unnecessary.)

Thiourea, 5% solution: Dissolve 10 g of thiourea (Analytical Reagent, Fisher Scientific Co.) in water and dilute to 200 ml.

n-Amyl alcohol: The *n*-amyl alcohol used must be free from oxidising agents such as peroxides. Test each new bottle before use by the addition of potassium iodide and starch solution to a dilute hydrochloric acid wash of the alcohol. If the presence of peroxides is indicated distil according to the method described by Russel and Hart[9] for iso-amyl alcohol. Analytical reagent *n*-amyl alcohol obtained from Mallinckrodt Chemical Works was found to be free from peroxides.

Chloroform: Analytical reagent, obtained from Fisher Scientific Co.

General experimental procedure

Calibration curve. Pipette 20 ml of 25% ammonium tartrate solution, 40 ml of 5% boric acid solution, 20 ml of 10% ascorbic acid solution, and 10 ml of 10% hydroxylamine hydrochloride solution into a 250-ml beaker. Adjust the pH of the resulting "base" solution to 5·5 with concentrated ammonia solution using a pH meter, and dilute to volume with water in a 200-ml volumetric flask. Add a 20-ml aliquot of this solution to each of six 60-ml separatory funnels which are marked at 25 ml. Then, by burette, add to the last five funnels 1, 2, 3, 4 and 5 ml, respectively, of the pre-reduced standard iron solution. The first funnel contains the blank. Dilute the contents of each funnel to the 25-ml mark with water and swirl to mix. (Because *n*-amyl alcohol and water are soluble in each other to a certain extent the total volume should be carefully controlled.) Add to each funnel 2 ml of 5% thiourea solution, mix and allow to stand for 5 min. Add 4 ml of 0·001 *M* bathophenanthroline solution, mix and allow to stand for 15 min. Then add, by pipette, 10 ml of *n*-amyl alcohol, stopper and shake for 2 min. Allow 5 min for the layers to separate, then drain off and discard the lower aqueous layer. Drain the *n*-amyl alcohol extracts into 15-ml centrifuge tubes and centrifuge for 30 sec. Determine the absorbance of each extract against the blank as the reference solution, using 1-cm cells in a Beckman DU spectrophotometer, at a wavelength of 536 mμ. Plot micrograms of iron *vs.* absorbance.

Procedure for niobium, tantalum, molybdenum and tungsten metals. In the following procedure a reagent blank is carried along with the samples.

Transfer a 0·5000-g sample of the powdered metal to a 250-ml Teflon beaker (tetrafluoroethylene-Dynalab Corp., Rochester, N.Y.), add 5 ml of water and 2 ml of hydrofluoric acid (plastic pipette) and cover the beaker with a Teflon watch glass. Then through the lip of the beaker add concentrated nitric acid slowly, 10 drops at a time, until all of the metal is in solution. Usually 1 or 2 ml is sufficient. If a small portion of the sample remains undissolved at this stage, heat gently on the hot plate until in solution. (If all of the sample does not go into solution with the above procedure, then omit the preliminary addition of the 5 ml of water and dissolve directly with the hydrofluoric and nitric acids). Remove the Teflon cover and wash down the sides of the beaker with a small amount of water. (For molybdenum metal and a separate reagent blank, add at this point, 2 ml of concentrated hydrochloric acid and heat until the dark brown coloration disappears and the solution becomes pale yellow). Add 3 ml of formic acid to destroy excess nitric acid[10] and heat gently until the evolution of oxides of nitrogen ceases. Wash down the sides of the beaker with a minimum amount of water and evaporate to approximately 5 ml. Add 10 ml of water and 10 ml of 25% ammonium tartrate solution, and heat gently without boiling for 5–10 min, at which point the solution should be clear. Add 20 ml of 5% boric acid solution and allow to stand for 20 min. (If the iron determination cannot be completed the same day, allow to stand overnight at this point.) Add 2 ml of 1:1 sulphuric acid, mix, and add 10 ml of 10% ascorbic acid solution and 5 ml of 10% hydroxylamine hydrochloride solution. Mix, allow to stand for 10 min, then adjust the pH to 5·5 with concentrated ammonia solution using a pH meter. Transfer to a 100-ml volumetric flask and dilute to volume. Transfer a suitable aliquot (4-20 ml) of both sample and blank solutions, depending on the iron concentration of the sample, to 60-ml separatory funnels. Dilute to the 25-ml mark with water and proceed with the iron extraction as described for the calibration curve. Measure the absorbance of the sample against the reagent blank and determine the iron content of the aliquot by reference to the calibration curve. 1 μg of iron = 0·001% when 20-ml aliquots of sample are taken.

RESULTS

Extraction of the coloured complex

Although the iron[II]-bathophenanthroline complex can be extracted into various organic solvents,[6] *n*-amyl alcohol was chosen for the present work because of its ready availability.

In preliminary experiments with pure iron solutions, it was found that up to 25 μg of iron contained in a 25-ml volume of solution could be extracted quantitatively over the pH range 3 to 7 in a single stage with 10 ml of *n*-amyl alcohol. The extraction of

larger amounts of iron was not attempted because of the high optical density of the resulting extract.

Factors influencing formation of the iron complex and its subsequent extraction from solutions of the high-purity metals

Reductant. Hydroxylamine hydrochloride is often used for the reduction of iron^{III} in spectrophotometric procedures. However, when the effectiveness of this reducing agent was tested on samples of niobium, tantalum, molybdenum and tungsten metals which were decomposed according to the described procedure, and to which standard additions of iron had been made, excessive time (up to 4 hr) was required for complete reduction of the iron.

Ascorbic acid was tested under similar conditions as a possible reductant and the results of these experiments indicated that this reagent was capable of reducing iron more rapidly than hydroxylamine hydrochloride. However, after the iron^{II}-bathophenanthroline complex was extracted into *n*-amyl alcohol, there was a tendency for the colour to fade. This was considered to be caused by low solubility of ascorbic acid in *n*-amyl alcohol and the consequent atmospheric oxidation of the iron^{II} complex.

Because the organic extracts from the tests previously performed with hydroxylamine hydrochloride showed no inclination for colour fading over a 24 hr period, it was considered that a mixture of hydroxylamine hydrochloride and ascorbic acid would be effective in bringing about immediate and complete reduction of iron and producing a stable extract. A series of tests performed on synthetic solutions of the metals employing the two reducing agents showed that the above conditions were fulfilled.

Effect of pH. Experiments to determine the effect of pH on the formation and extraction of the iron^{II}-bathophenanthroline complex from solutions of the high-purity metals, were performed with molybdenum solutions, because it was considered that the optimum conditions for determining iron in molybdenum metal would also be applicable to the other three metals. Because many bathophenanthroline methods for iron recommend a pH of 4 or 5·5[6,8,11,12,13] for the extraction of the iron complex, tests were carried out at both pH values on synthetic samples prepared by decomposing 0·5-g portions of molybdenum metal of low iron content according to the described dissolution procedure. Known additions of iron were made after the formic acid treatment, followed by the amounts of ammonium tartrate, boric acid, and reducing agents specified in the proposed procedure. After adjusting the pH, the solutions were diluted to the mark with water in 100-ml volumetric flasks. Appropriate aliquots of the resulting solutions were made up to 25 ml with water, 4 ml of 0·001 *M* bathophenanthroline solution[6] were added, and the iron complex was extracted with 10 ml of *n*-amyl alcohol. The total iron content of these solutions was determined by reference to calibration curves prepared from "base" solutions of the same pH (described under *Calibration Curve*). The results of these tests are given in Table I.

Table I shows that the recovery of iron from molybdenum solutions is incomplete when the iron complex is formed and extracted at pH 4, but at pH 5·5 total recovery of the added iron was obtained indicating complete reduction and complete formation of the iron complex.

Tests carried out at pH 5·5 on synthetic niobium, tantalum and tungsten samples

showed that complete recovery of the added iron was obtained for the niobium and tungsten samples, but the results for the tantalum samples were low. Tests performed with tantalum solutions adjusted to pH 4 and pH 7 also yielded low results. However, when more bathophenanthroline was added to the aqueous phase remaining after extraction of these solutions, increased colour formation was observed after several

TABLE I.—EFFECT OF pH ON EXTRACTION OF IRON FROM SYNTHETIC MOLYBDENUM SAMPLES

Sample	Fe found, %	
	pH 4	pH 5·5
Mo	0·0079	0·0083
Mo + 0·010% Fe	0.0176	0·0182
Mo + 0·025% Fe	0·0311	0·0335
Mo + 0·050% Fe	0·0438	0·0575
Mo + 0·100% Fe	0·0880	0·1085

hr, indicating that prior to the extraction step the reduction of the added iron was incomplete. Further investigation with tantalum solutions showed that this was because of the pH at which the reducing agents were added. The pH of the sample solutions after dissolution according to the described procedure and addition of ammonium tartrate and boric acid was found to be approximately 3. At this pH reduction of iron was complete in niobium, molybdenum and tungsten solutions, but was incomplete in tantalum solutions. However, when the pH was lowered to 1 with sulphuric acid before reduction, complete recovery of the added iron was obtained.

The results of the foregoing experiments show that the development of a single method for determining iron which would be applicable to all four metals described, would require that reduction takes place at approximately pH 1 followed by pH adjustment to 5·5 for the formation and extraction of the iron complex.

Effect of diverse metal ions

Smith, McCurdy and Diehl[8] state that bathophenanthroline is more or less specific for iron and that the only metal cations which form bathophenanthroline derivatives are copper and cobalt, which do not interfere under the conditions of their procedure. Cobalt is described as forming a light yellow complex which is not extracted from acid solution. Copper also forms a yellow derivative, copper^{I}-bisbathophenanthroline, in neutral or alkaline solution, which is transformed on acidifying the solution to colourless copper^{I}-monobathophenanthroline. They state further, that at pH 4 the copper^{I}-mono derivative is extracted but is colourless, and that copper, in quantities up to 250 μg, does not interfere.

More recent investigations have shown that bathophenanthroline is not specific for iron. Guest and Roloson[12] in determining iron in uranium-bearing materials employing hydroxylamine hydrochloride as reductant, found that copper is a very serious interferent at pH 4, and that bathophenanthroline forms a copper complex in preference to the iron complex. Gahler *et al.*[3] found that copper, cobalt, nickel and manganese interfere to the extent that they consume reagent. Tests carried out in this laboratory corroborated these results and showed that cadmium and zinc also interfere.

Preliminary tests with copper were carried out at pH 4 as recommended by Smith *et al.*[8] Varying amounts of copper solution and a constant known amount of pre-reduced iron solution were added to aliquots of "base" solution which had been adjusted to pH 4. (Reduction of the iron prior to addition to the "base" solution ensures that all of the iron will be present in the reduced form at the given pH). After diluting the resulting solutions to 25 ml with water, 4 ml of 0·001 *M* bathophenanthroline solution were added and the iron complex was then extracted with 10 ml of *n*-amyl alcohol. The results of these tests (Table II) show the magnitude of the copper interference. At the concentration of bathophenanthroline employed, as little as 5 μg of copper will enhance the iron result, and at higher levels (250 μg) the bathophenanthroline is preferentially complexed by the copper. Amounts of copper in excess of 250 μg were found to give negative absorption readings.

TABLE II.—EFFECT OF COPPER ON EXTRACTION OF IRON WITH BATHOPHENANTHROLINE AT pH 4†

Cu taken, μg	Fe found, μg
5	10·9
10	11·4
25	13·2
50	16·0
100	20·7
250	1·0*

* Bathophenanthroline preferentially complexed by copper.
† Concentration of iron present: 10 μg.

The possibility that the four high-purity metals under consideration could contain trace amounts of copper had to be taken into account; consequently, some means was required for complexing copper and preventing its reaction with bathophenanthroline. It is known that small amounts of copper can be masked with thiourea,[14] therefore this reagent was investigated as a possible complexing agent. The tests described in the preceding paragraph were repeated with the addition of thiourea prior to the addition of the bathophenanthroline. The results of these tests (Table III) show that for small amounts of copper, thiourea successfully inhibits the formation of the copper^{I}-bathophenanthroline complex.

TABLE III.—EFFECT OF THIOUREA ON THE EXTRACTION OF IRON IN THE PRESENCE OF COPPER AT pH 4

Cu taken, μg	Fe found, μg
10	10·2
25	10·1
50	10·1
100	10·1
250	10·7

Concentration of iron present: 10 μg.
Amount of thiourea added: 0·100 g.

The effectiveness of thiourea in eliminating interference from copper was tested for concentrations of iron up to 25 μg at pH 5·5, because this is the pH required for extracting iron from solutions of the four high-purity metals. Results show (Table IV) that up to 50 μg of copper can be tolerated in test solutions at this pH.

TABLE IV.—EFFECTIVENESS OF THIOUREA IN COMPLEXING COPPER AT pH 5·5

Fe taken, μg	Fe found, μg	
	Cu taken, 100 μg	Cu taken, 50 μg
0	0·3*	0·2*
5	5·3†	5·3
10	9·9	10·2
15	14·5	14·9
20	18·7	19·6
25	23·5	24·5

* Extracts were yellow.
† Extract had a slight orange tinge.

Tests carried out with cobalt, cadmium, nickel, manganese and zinc showed that their interference effects are not as serious as that from copper. No attempt was made to find ways of eliminating these elements because spectrographic results on 22 samples of high-purity niobium, tantalum, molybdenum and tungsten metals showed these impurities and also copper to be present in small amounts, *i.e.* less than 0·01 %. The determination of the quantity of each impurity which could be tolerated at the bathophenanthroline concentration used in the proposed procedure would have little significance with regard to the present investigation because small amounts of each impurity do occur in the same sample. Therefore, tests were carried out to determine the maximum amount of the six interfering elements which could be present together in equal amounts in solutions of the four metals without affecting the iron results. Solutions of the high-purity metals were prepared as described under *General Experimental Procedure*. Then, varying quantities of a solution containing equal amounts of copper, cobalt, cadmium, nickel, manganese and zinc were added to three 20-ml aliquots of each of these solutions, and the total iron content of the resulting aliquots was determined as described in the proposed method. Also, in order to determine the effect of the combined interfering elements at levels of iron greater than are present in the metals themselves, and approaching the upper limit of the calibration curve, the above tests were repeated with the addition of a known amount (15 μg) of standard pre-reduced iron solution. Table V gives the results of these tests for niobium only, and also the results of tests carried out in an identical manner with 50 μg of copper alone which was previously shown (Table IV) to have no appreciable effect in test solutions. Tests performed with tantalum, molybdenum and tungsten solutions under the same conditions yielded similar results.

The results in Table V and also those obtained with synthetic tantalum, molybdenum and tungsten samples show that in samples of the four metals analysed according to the proposed procedure, up to 50 μg of copper alone, or 10 μg each of copper, cobalt, cadmium, nickel, manganese, and zinc may be present together in the aliquot taken for extraction without appreciably affecting the iron result. These

TABLE V.—EFFECT OF INTERFERING CATIONS ON THE DETERMINATION OF IRON BY THE PROPOSED METHOD IN SYNTHETIC NIOBIUM SAMPLES

Sample	Total Fe present, %	Fe found, %
Nb + 0·005% each of Cu, Co, Cd, Ni, Mn, Zn	0·0064 (4)	0·0063
Nb + 0·01%* each of Cu, Co, Cd, Ni, Mn, Zn	0·0064	0·0062
Nb + 0·02% each of Cu, Co, Cd, Ni, Mn, Zn	0·0064	0·0062
Nb + 0·015%* Fe + 0·005% each of above	0·0214	0·0213
Nb + 0·015% Fe + 0·01% each of above	0·0214	0·0208
Nb + 0·015% Fe + 0·02% each of above	0·0214	0·0185
Nb + 0·05%* Cu	0·0064	0·0063
Nb + 0·015% Fe + 0·05% Cu	0·0214	0·0212

Figure in parenthesis indicates number of replicate determinations.

* 10, 15 and 50 μg, respectively, for 20-ml extraction aliquots.

tolerance limits are adequate for the level of these impurities present in high-purity samples of the four metals, but they could be increased somewhat by increasing slightly the thiourea and bathophenanthroline concentrations. However, experiments performed with molybdenum solutions using 0·100 and 0·250 g of thiourea in combination with 2 ml of a 0·01*M* solution of bathophenanthroline in ethyl alcohol were unsuccessful. The extracts obtained were milky in appearance and did not clear on being centrifuged.

Application to synthetic niobium, tantalum, molybdenum and tungsten samples for iron contents up to approximately 0·1%

In order to determine its accuracy for higher levels of iron concentration, the proposed method was applied to the analysis of a series of synthetic samples in which the added iron concentration varied from 0·01 to 0·10%, and which were prepared from the same four metals used in the preceding tests. The standard iron solution was added after the formic acid treatment. The results obtained are given in Table VI.

TABLE VI.—RECOVERY OF IRON BY THE PROPOSED METHOD FROM SYNTHETIC NIOBIUM, TANTALUM, MOLYBDENUM AND TUNGSTEN SAMPLES

Sample	Total Fe present, %	Fe found, %	Sample	Total Fe present, %	Fe found, %
Nb + 0·010% Fe	0·0164	0·0167	Ta + 0·010% Fe	0·0166	0·0163
Nb + 0·025% Fe	0·0314	0·0314	Ta + 0·025% Fe	0·0316	0·0318
Nb + 0·050% Fe	0·0564	0·0568	Ta + 0·050% Fe	0·0566	0·0562
Nb + 0·100% Fe	0·1064	0·1089	Ta + 0·100% Fe	0·1066	0·1060
Mo + 0·010% Fe	0·0179	0·0174	W + 0·010% Fe	0·0156	0·0166
Mo + 0·025% Fe	0·0329	0·0330	W + 0·025% Fe	0·0306	0·0310
Mo + 0·050% Fe	0·0579	0·0555	W + 0·050% Fe	0·0556	0·0563
Mo + 0·100% Fe	0·1079	0·1064	W + 0·100% Fe	0·1056	0·1070

DISCUSSION

Table VI shows that the results obtained by the proposed bathophenanthroline method agree favourably with the total calculated percentage of iron present in the range of values up to approximately 0·1%.

In the proposed procedure the iron^{II}-bathophenanthroline complex is extracted in a single stage with a fixed quantity of *n*-amyl alcohol. Because *n*-amyl alcohol is soluble to a certain degree in water, the absorbancy of the resulting extract therefore depends on the density and volume as well as the pH of the aqueous phase remaining after extraction. Therefore, preparation of a suitable calibration curve for determining iron in the four high-purity metals would require that extraction of known amounts of iron for plotting the reference curve should take place under essentially the same conditions as the iron is extracted in the samples. The use of a pre-reduced standard iron solution together with 20-ml aliquots of a "base" solution adjusted to pH 5·5, and consisting of the reagents required in the sample preparation, ensures that the sample conditions regarding reduction and extraction pH's and density and volume of the aqueous phase, will be duplicated in the calibration solutions for amounts of iron up to 0·025%. The presence of greater than 0·025% iron in samples of the four metals necessitates extraction of a smaller aliquot of the sample solution than 20 ml. Dilution of a smaller aliquot to 25 ml with water prior to extraction of the iron complex is accompanied by a variation in pH and density, and if extremely accurate analysis is required, the absorbancy of the resulting extract should be determined by reference to a calibration curve prepared by using the same size aliquot of the "base" solution. However, when a 4-ml aliquot of sample solution is diluted to 25 ml with water the density diminishes, and the pH decreases from 5·5 to approximately 4·6. These combined effects were shown to produce a maximum positive error of 0·002% at the 0·10-% iron level in test solutions when extraction was carried out at pH 4·6. This is felt to be within the experimental error of the method.

The proposed procedure is suitable for samples containing between 0·001 and 0·125% of iron, but material containing larger amounts could also be successfully analysed simply by reducing the initial sample weight. The method is extremely sensitive, the technique required is simple, and results are reproducible under routine conditions.

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Zusammenfassung—Eine spektrophotometrische Methode zur Bestimmung von Eisenspuren in hochreinem Niob, Tantal, Molybdän und Wolfram wird beschrieben. Nach Lösen der Probe wird Eisen mittels Ascorbinsäure und Hydroxylamin reduziert, der rote Komplex mit Bathophenanthrolin (4,7-Diphenyl-10-phenanthrolin) wird geformt, in n-Amylalkohol ausgeschuttelt und die Absorbtion bei 536 mμ gemessen. Störungen durch Kupfer werden mittels Thioharnstoff ausgeschaltet. Co, Cd, Ni, Mu und Zn stören ebenfalls, doch sind die in hochreinen Metallen vorhandene Mengen so gering, dass der Einfluss vernachlässigt werden kann. Die Resultate sind sehr präzise, wenn die Einstellung des pH der Lösung während Reduktion und Extraktion genau bewerkstelligt wird.

Résumé—Les auteurs décrivent une méthode spectrophotométrique de dosage de traces de fer dans le niobium, le tantale, le molybdène et le tungstène de haute pureté. Après mise en solution de l'échantillon et réduction du fer à l'état(II) par l'acide ascorbique et le chlorhydrate d'hydroxylamine, le complexe rouge formé entre le fer ferreux et la bathophénanthroline (4,7-diphényl-1,10-phénanthroline) est extrait

par l'alcool amylique. La mesure est effectuée à 536 mμ. L'interférence du cuivre peut être éliminée par la thiourée. Le cobalt, le cadmium, le nickel, le manganèse et le zinc genent également mais les quantités de chacune de ces impuretés présentes dans les quatre métaux de haute pureté considérés sont si faibles que leur influence est négligeable. Des résultats reproductibles et précis peuvent être obtenus par un contrôle soigné du pH lors de la réduction et de l'extraction.

REFERENCES

[1] Jane Hastings, T. A. McClarity and E. J. Broderick, *Analyt. Chem.*, 1954, **26**, 379.
[2] R. H. A. Crawley and M. L. Aspinal, *Analyt. Chim. Acta*, 1955, **13**, 376.
[3] A. R. Gahler, R. M. Hamner and R. C. Shubert, *Analyt. Chem.*, 1961, **33**, 1937.
[4] W. R. Schoeller, *Analytical Chemistry of Tantalum and Niobium*. Chapman and Hall, London, 1937.
[5] J. D. H. Strickland, *J. Amer. Chem. Soc.*, 1952, **74**, 862.
[6] H. Diehl and G. F. Smith, *The Iron Reagents*. G. Frederick Smith Chemical Co., Columbus, Ohio, 1960.
[7] F. H. Case, *J. Org. Chem.*, 1951, **16**, 1541.
[8] G. F. Smith, W. H. McCurdy, Jr. and H. Diehl, *Analyst*, 1952, **77**, 418.
[9] G. Russel and P. J. Hart, *ibid.*, 1958, **83**, 202.
[10] C. L. Luke, *Analyt. Chem.*, 1953, **25**, 148.
[11] W. M. Banick and G. Frederick Smith, *Analyt. Chim. Acta*, 1957, **16**, 464.
[12] R. J. Guest and F. P. Roloson, *The Determination of Iron in Uranium-Bearing Materials by use of an Ethyl Acetate Extraction and a Colorimetric Bathophenanthroline Procedure*. Radioactivity Division, Dept. of Mines and Technical Surveys, Ottawa, Topical Report No. TR-137/57, 1956.
[13] M. J. Seven and R. E. Peterson, *Analyt. Chem.*, 1958, **30**, 2016.
[14] M. Zeigler, O. Glemser and N. Petri, *Z. analyt. Chem.*, 1957, **154**, 81.

Talanta, 1962, Vol. 9, pp. 1037 to 1041. Pergamon Press Ltd. Printed in Northern Ireland

PRECIPITATION FROM MIXED SOLVENTS—I
ALUMINIUM 8-HYDROXYQUINOLATE

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Summary—The precipitation of aluminium 8-hydroxyquinolate from a buffered acetone–water system has been effected by the volatilisation of the acetone. The use of this procedure results in a precipitate with physical characteristics superior to that obtained in the conventional manner and allows more efficient separation from interfering cations. Separations of 10-mg quantities of aluminium from an equal amount of cadmium as well as separations of 25-mg quantities of aluminium from at least 420 mg of magnesium and twice that amount of calcium can easily be accomplished. These results compare favourably with those obtained by hydrolysis of 8-acetoxyquinoline. A procedure is described for the quantitative determination of 2–10 mg of aluminium.

THAT controlled precipitation can lead to increased crystallinity, greater ease of handling and greatly improved separation from diverse ions has long been known. For these reasons the method of slow, direct addition of precipitants has given way, in many cases, to the methods of precipitation from homogeneous solution (PFHS).[1] In the case of the precipitation of aluminium with 8-hydroxyquinoline, such techniques as the *in situ* generation of the precipitant by hydrolysis of 8-acetoxyquinoline[2,3] and the gradual reduction of solubility by a slow pH change[4] have been employed. In general, the application of such techniques has been restricted by the disadvantages that (1) some of the reagents used for the *in situ* generation are relatively exotic and expensive, (2) the rate of the *in situ* generation is usually pH-dependent as is the solubility of the final precipitate, and there may not be a range where these two characteristics both have useful values, or (3) when the pH is changed over a large range to effect the precipitation of the desired ion it also effects the precipitation of undesired diverse ions.

The method herein described is based upon the observation that the presence of relatively large amounts of miscible organic solvents retards the precipitation of certain materials, particularly chelated metallic ions. Volatilisation of the organic component then leads to the precipitate eventually displaying only its aqueous solubility. In a preliminary report on this work[5] it was shown that the employment of this technique permitted the direct addition of the precipitant and that the subsequent volatilisation of the organic solvent from the buffered solution effected the gradual formation of the precipitate. In this manner the advantages of the more conventional forms of PFHS were retained while the disadvantages which have been mentioned were eliminated.

In this paper the general utility of precipitation from a mixed solvent system was investigated as it applied to the case of aluminium 8-hydroxyquinolate. This system was chosen since it permitted comparisons with the conventional means of precipitation and with the earlier method of precipitation by the controlled hydrolysis of the

8-acetoxyquinoline. Of particular interest are comparisons relating to the physical characteristics of the precipitate and comparisons of separations from diverse ions.

EXPERIMENTAL

Reagents

Aluminium: An aluminium solution was prepared from reagent-grade $AlK(SO_4)_2 \cdot 12H_2O$ (Fisher Scientific Company, Fair Lawn, New Jersey). A value of 9·99 ± 0·03 mg of aluminium per 10 ml of solution was obtained by conventional precipitation of the aluminium with 8-hydroxyquinoline.[6]

Cadmium: A solution containing 1 mg of cadmium per ml was prepared by weighing C.P. Grade $Cd(NO_3)_2 \cdot 4H_2O$ (Fisher Scientific Company, Fair Lawn, New Jersey).

Magnesium: A solution containing 300 mg of magnesium per 25 ml was prepared by weighing Reagent-grade $MgSO_4 \cdot 7H_2O$ (Fisher Scientific Company, Fair Lawn, New Jersey).

Calcium: A solution containing 1000 mg of calcium per 25 ml was prepared by weighing Reagent grade $Ca(NO_3)_2 \cdot 4H_2O$ (J. T. Baker Chemical Company, Phillipsburg, New Jersey).

8-Hydroxyquinoline: A 5% solution in 2*N* acetic acid was prepared by adding 5·7 ml of glacial acetic acid to 2·50 g of the reagent-grade material (Fisher Scientific Company, Fair Lawn, New Jersey); after a gentle warming and agitation to dissolve the reagent, the solution was diluted to 50 ml with distilled water. In some cases it was desired to add this reagent without introducing further acid into the system. In these instances a solution was prepared by dissolving 10 g of 8-hydroxyquinoline in 90 ml of acetone.

All other chemicals were reagent-grade. It was noted that certain lots of reagent-grade acetone required distillation in order to remove an unidentified water-insoluble residue.

Apparatus

A Beckman Model G pH meter equipped with glass and calomel electrodes was used for all pH measurements.

Procedure

Aluminium precipitation: Samples of 2 to 10 ml of the aluminium solution (containing approximately 2 to 10 mg of aluminium) were mixed with 50 ml of distilled water in a 250-ml beaker. To this solution were added 60 ml of acetone, 4 ml of the 5% 8-hydroxyquinoline solution, and 40 ml of 2*N* ammonium acetate. The resulting solution was placed on a water bath at 70–75° and left uncovered for 3 hr. Visible precipitation began in about 15 min. At the end of the evaporation period the samples were removed from the bath, allowed to cool, and filtered through medium-porosity sintered-glass crucibles. The precipitates were washed three times with distilled water and dried for 3 hr at 135–140°; the product was weighed as anhydrous $Al(C_9H_6ON)_3$. The pH of the filtrates was found to lie in the range 5·5–5·6.

Analysis of ten samples of 10 ml each by this method yielded an average value of 9·97 mg of aluminium with a standard deviation of 0·03 mg. In addition, samples of from 2 to 10 ml were analysed with the results summarised in Table I.

Cadmium co-precipitation: In order to study the effect of pH upon the co-precipitation of cadmium various amounts of sodium acetate–acetic acid or ammonium acetate–acetic acid solutions were added to solutions containing approximately 10 mg of aluminium and 10 mg of cadmium. The resulting solutions were either diluted to 175 ml and precipitated by the addition of 8-hydroxyquinoline according to the conventional method[6] or were treated with 60 ml of acetone, 3 ml of a 10% solution of 8-hydroxyquinoline in acetone and sufficient water to bring the total volume to 175 ml.

TABLE I.—QUANTITATIVE DETERMINATION OF ALUMINIUM FROM A WATER-ACETONE MIXTURE

Aluminium added, *mg*	Aluminium precipitated, *mg*
1·99	1·98
3·99	4·02
4·99	4·98
5·98	6·00
6·98	7·00
7·98	8·00
9·97	10·04

Average error 0·03 mg

Samples treated by the second method were then heated for 3 hr at 70–75°, filtered, dried and weighed as before. In both methods of treatment sufficient precipitant was added to provide a 20% excess of 8-hydroxyquinoline over that required to precipitate completely both aluminium and cadmium and in both methods the values of the final pH of the filtrates were measured. Figure 1 presents the results obtained in this manner. Additional studies were then made in the pH range 4·7–4·9, using solutions which contained 10 ml of the aluminium solution and 10, 15 or 20 ml of the cadmium solution. To these mixtures were added 60 ml of acetone, 20 ml of 5*N* acetic acid, 40 ml of 3*M* sodium acetate and 5·5 ml of 5% 8-hydroxyquinoline in acetone. The resulting solutions were treated as before and the results are included in Table II.

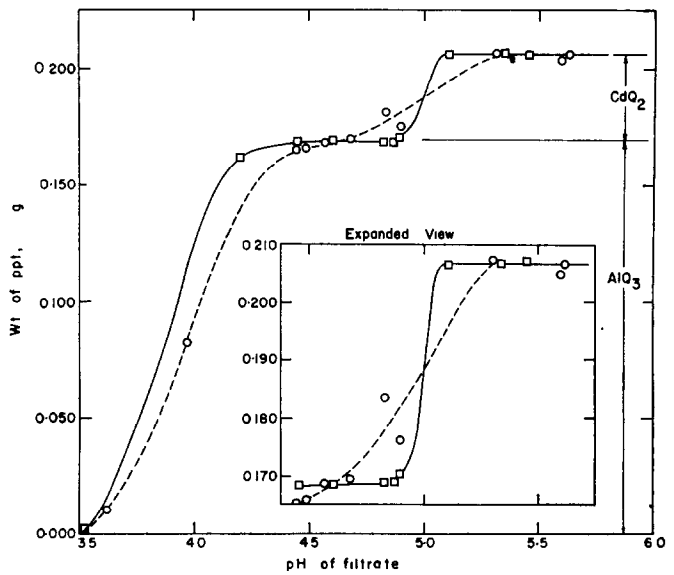


FIG. 1.—Weight of precipitate, g, versus pH of filtrate.
□ Evaporation method. ○ Direct addition method.

TABLE II.—EFFECT OF DIVERSE CATIONS ON ALUMINIUM DETERMINATION FROM A WATER–ACETONE SYSTEM

Aluminium present, *mg*	Diverse ion added	Weight of diverse ion, *mg*	Weight of diverse ion precipitated, *mg*
10	Cd	10	<0·1*
10	Cd	15	7·3*
10	Cd	20	13·0*
25	Mg	240	<0·1
25	Mg	300	<0·1
25	Mg	360	<0·1
25	Mg	420	<0·1
25	Ca	800	<0·1
25	Ca	1000	5·5
25	Ca	1200	1·4
25	Ca	1400	2·0

* Average of two samples. Filtrate pH of 4·8.

Magnesium co-precipitation: Twenty-five ml of the standardised aluminium solution were treated essentially as described in the aluminium procedure, except that 240–420 mg of magnesium were added. In addition, there was added a 20% excess of 8-hydroxyquinoline over that required to precipitate aluminium completely. Fifty ml of 2*M* ammonium acetate were used as a buffer. The values of pH for the filtrates were 5·2–5·3, and the results are included in Table II.

Calcium co-precipitation: Twenty-five ml of the standardised aluminium solution were treated essentially as described in the aluminium procedure, except that 800–1400 mg of calcium were added. In addition, there was added a 20% excess of 8-hydroxyquinoline over that required to precipitate aluminium completely. Fifty ml of 2*M* ammonium acetate were used as a buffer. The values of pH for the filtrates were 5·1–5·2, and the results are included in Table II.

RESULTS AND DISCUSSION

Precipitation of 2–10 mg of aluminium by this method gives quantitative results, and a highly crystalline precipitate is produced, which is much more easily filtered and washed than that obtained by conventional methods. In these respects the precipitates obtained by the evaporation method closely paralleled those obtained by the hydrolysis of 8-acetoxyquinoline. The use of 24·98-mg samples of aluminium also yields quantitative results, even in the presence of a large excess of magnesium or calcium, and despite the fact that rather high concentrations of the precipitating agent were present.

The results of the cadmium co-precipitation study are shown in Fig. 1. It should be noted that for this study two highly interfering ions were chosen to illustrate the effectiveness of the method of precipitation from mixed solvents in reducing co-precipitation. The curve obtained using the conventional method of direct addition shows no distinct break, and no pH at which separation is possible. Although the useful pH range is not wide, the proposed method of precipitation from mixed solvents should permit the separation of 10 mg of aluminium from 10 mg of cadmium at pH's between 4·7 and 4·9. The results in Table II show this to be the case when samples are analysed by the method described in the cadmium procedure. These separations are comparable with, if not better than, those obtained by PFHS utilising the hydrolysis of 8-acetoxyquinoline when 1·8 mg of cadmium was precipitated from a sample containing 10 mg of aluminium and 10 mg of cadmium.[2] Under the same conditions the direct addition method precipitated 2·7 mg of the cadmium.

The results of the magnesium and calcium co-precipitation studies are shown in Table II. These results are comparable to those recently obtained by hydrolysis of 8-acetoxyquinoline.[3]

Upon the addition of the acetone to the water-aluminium-calcium mixture the solution became quite cloudy, probably because of the decreased solubility of the inorganic salts in the resultant water-acetone mixture. The subsequent addition of 8-hydroxyquinoline and ammonium acetate solutions did not noticeably affect this cloudiness and only after prolonged heating at the evaporation temperature (70–75°) did the solutions become clear. Even under these rather adverse conditions the separation of aluminium from calcium was highly effective.

The behaviour of the water-aluminium-magnesium mixture upon the addition of acetone was similar to that of the system containing calcium, with the exception that a very brief heating at 60–65° was sufficient to remove all turbidity.

CONCLUSIONS

The results presented clearly illustrate the utility of the method of precipitation from mixed solvents in the analysis of aluminium. This method not only yields precipitates of superior physical characteristics to those obtained by the conventional method, but also permits the selection of any desired pH without concern about the possibility of altering the rate of the precipitation. In addition it has been possible to

achieve these improvements while using only equipment and reagents commonly available in most laboratories.

Additional work with other cations, precipitants, and solvent systems is under way, and will be the subject of future papers.

Acknowledgement—The authors gratefully acknowledge the financial support of the Research Corporation, of the Atomic Energy Commission under contract AT(40-1)-2954 and of the American Oil Company who sponsored the fellowship held by one of the authors.

Zusammenfassung—Die Fällung von Al-Oxinat aus gepufferter Azeton-Wasserlösung durch Verdampfen des Azetons wird beschrieben. Ein Niederschlag mit stark verbesserten physikalischen Eigenschaften wird erhalten. Trennung von 10 mg Al von einer gleichen Menge Cd und Trennung von 25 mg Al von mindestens 420 mg und zweimal soviel Ca kann leicht bewerkstelligt werden. Die Ergebnisse lassen sich sehr wohl mit denen vergleichen, die nach der Methode der Hydrolyse von 8-Azetoxychinolin erhalten werden. Eine Arbeitvorschrift zu Bestimmung von 2–10 mg Al wird mitgeteilt.

Résumé—La précipitation de l'oxinate d'aluminium à partir d'un mélange eau–acétone au milieu tamponné a été effectuée par volatilisation de l'acétone. Le procédé permet d'obtenir un précipité dont les caractéristiques physiques sont supérieures à celles obtenues par la méthode traditionnelle et conduit à une séparation plus efficace. La séparation de 10 mg d'aluminium d'une quantité égale de cadmium, ou de 25 mg d'aluminium d'au moins 420 mg de magnésium et deux fois cette quantité de calcium peut être effectuée aisément. Ces résultats se comparent favorablement à ceux obtenus par l'hydrolyse de la 8-acétoxyquinoléine. Une méthode est décrite pour le dosage quantitatif de 2 à 10 mg d'aluminium.

REFERENCES

[1] L. Gordon, M. L. Salutsky and H. H. Willard, *Precipitation from Homogeneous Solution.* John Wiley Sons, Inc., New York, 1959.
[2] L. Howick and W. Trigg, *Analyt. Chem.*, 1961, **33**, 302.
[3] D. J. Marec, E. D. Salesin and L. Gordon, *Talanta*, 1961, **8**, 293.
[4] K. E. Stumpf, *Z. analyt. Chem.*, 1953, **138**, 30.
[5] L. Howick and J. Jones, *Talanta*, 1961, **8**, 445.
[6] A. R. Olson, C. W. Koch and G. C. Pimentel, *Introductory Quantitative Chemistry.* W. H. Freeman and Company, San Francisco, 1956.

Talanta, 1962, Vol. 9, pp. 1043 to 1052. Pergamon Press Ltd. Printed in Northern Ireland

APPLICATION OF THE RADIOACTIVE IONISATION DETECTOR TO THE DETERMINATION OF PERMANENT GASES BY GAS CHROMATOGRAPHY AND SOME USES IN STUDIES OF CHEMICAL KINETICS

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Summary—It has been found possible to determine volumes of hydrogen, methane, and carbon dioxide within the range 0·1–1·0 ml at S.T.P. and carbon monoxide and nitrogen within the range 0·1–0·4 ml at S.T.P. with an accuracy of around 5% in a gas chromatograph using the radioactive ionisation detector, provided that the detector temperature and the rate of carrier gas flow through the column are maintained between stated limits. Results of experiments on the sensitivity of the instrument to oxygen, sulphur dioxide, ethane, propane and n-pentane are also reported. Particular attention has been directed towards selecting the most suitable parameter of the response peaks for use in quantitative analysis.

Some particular applications of the argon chromatograph in studies of chemical kinetics involving permanent gases are described, and a method for the removal of corrosive gases from mixtures to be analysed is discussed.

INTRODUCTION

THE radioactive ionisation detector (argon detector) for use in gas chromatography was originally developed for the determination of small amounts of those vapours which have an ionisation potential less than that of argon. Lovelock, who developed the detector,[1] has listed[2] some of the substances to which it does not respond normally, and these include hydrogen, nitrogen, oxygen, carbon dioxide and carbon monoxide. Lovelock also states[2] that the response of the detector to methane and to ethane is very much less than to the higher hydrocarbons. The simplicity and stability of the detector have made it desirable that the gases which it does not normally detect should be brought within its range, and a number of suggestions to this end have been made. Willis[3] has found that a controlled concentration of ethylene in the argon stream increases the sensitivity of the detector to the permanent gases; Berry[4,5] and Wiseman[6] have discussed the use of helium in ionisation detectors.

The present article discusses the determination of permanent gases in a standard argon detector, while avoiding the necessity for adding traces of ethylene to the gas stream or the added expense of using helium as the carrier gas. In addition to indicating the degree of accuracy which might be expected outside the range of substances for which the argon ionisation detector was designed, the present account is also concerned with some particular applications. A preliminary report on the use of the argon detector for the analysis of hydrogen-methane mixtures has already been given.[7] It is emphasised, however, that comparatively large volumes of permanent gases (0·1–1·0 ml at S.T.P.) must be used to obtain satisfactory responses. Since the disturbance peak on the introduction of each sample is very small, the instrument has

found particular application in kinetic studies in which it was necessary to analyse mixtures containing 2–4 components at intervals of 4–8 min.

EXPERIMENTAL

A diagrammatic sketch of the apparatus used to control argon flow and inject the sample is shown in Fig. 1. A sample of gas was connected through A to a McLeod gauge so that a known pressure of gas in the known volume B could be displaced into the previously evacuated sampling volume.

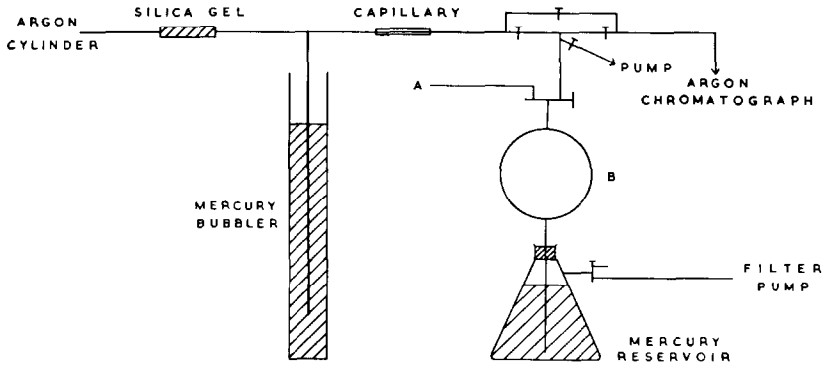


FIG. 1.—Apparatus used to inject samples into the argon gas stream.

Care was taken when making the apparatus that the glass around the tap (2 mm) in the sampling volume was shaped in such a way that gas bubbles were not trapped by the mercury, thus ensuring that the whole of the measured dose was swept from the sampling volume when the argon stream was deflected through it. The author used the apparatus to follow the kinetics of a gas-solid reaction occurring in a small reaction vessel attached at A, volumes being arranged so that 85–90% of the gas in the reaction vessel was withdrawn by a single stroke of the Toepler pump.

A standard Pye Argon Chromatograph was used throughout the work; the source contained radium-D but newer models now contain strontium-90. The rate of flow of cylinder argon (supplied by British Oxygen Co. Ltd.) was determined by the head of mercury in the bubbler and the capillary tube shown in Fig. 1. A single chromatographic column of charcoal (100–120 mesh B.S.S. standard screen) 80 cm long was used throughout almost all the work.

For quantitative calibrations of the chromatograph the following gases were used: cylinder hydrogen, purified by diffusion through heated palladium; cylinder nitrogen (oxygen free) passed through a liquid nitrogen trap; cylinder methane, carbon monoxide, carbon dioxide, ammonia and liquified sulphur dioxide, each condensed in liquid nitrogen, outgassed, the first-boiling fraction evacuated, and a sample withdrawn for study. All gases were shown to be free from appreciable amounts of impurities, by gas chromatographic analysis, before being studied in detail.

RESULTS

Unless otherwise stated, the response of the chromatograph refers to that found at 2000 v with a 10-mv bobbin in the recorder and the detector held at $20 \pm 2°$ with a flow of 30 ± 2 ml/min of argon through the 80-cm charcoal column, and "$\times 10$" scale of sensitivity of the detector. Deflections of the recorder in the same direction as that found for hydrocarbons (*e.g.*, benzene) will be termed "positive" and those in the opposite direction "negative".

Hydrogen

Sharp negative peaks were obtained (sketch given in ref. 7) and the most satisfactory parameter for quantitative studies was the distance from the maximum of the very small initial positive "kick" to the maximum of the large negative peak which immediately followed it, *i.e.*, the height of the steep front of the peak. Fig. 2 shows a composite plot of peak height against volume of hydrogen injected from 9 separate

sets of calibrations made at intervals over a period of 12 months. The scatter of results on Fig. 2 is greater than that observed on any set of calibrations made at any

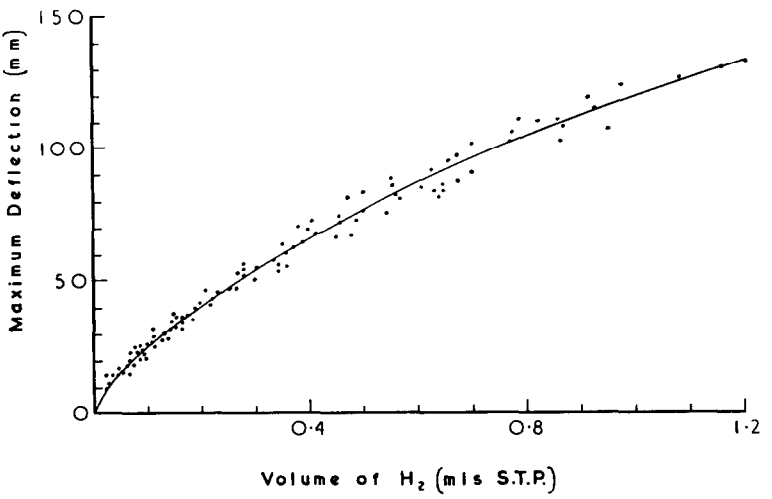


FIG. 2.—Calibration plot of maximum peak height of detector deflection against volume of hydrogen injected.

one time, because response tended to vary slightly over an extended period of time, and results from calibrations under slightly different sets of operating conditions have been included on Fig. 2. The following factors have been found to influence the peak height:

1. *The presence of air:* After the column was allowed to stand in air for some weeks, the sensitivity of the detector to hydrogen, under the same operating conditions used to determine the results on Fig. 2, showed a reduction of deflection from 20 mm at 0·1 ml to 30 mm at 1·0 ml at S.T.P. On another occasion the calibrations found immediately after regreasing the taps of the apparatus gave deflections less than those expected from Fig. 2. The degree of reproducibility of calibrations was considerably increased through baking out the column to 200° in an argon stream and cooling overnight in argon. This was repeated every night during quantitative work.

2. *Temperature:* Calibration curves at 24° and 29°, under otherwise identical conditions, were similar in shape, but the maximum deflections at 24° were some 5–7 mm less than those at the higher temperature for samples 0·1–1·0 ml at S.T.P.

3. *Argon flow rate:* A calibration plot at a flow of 17 ml/min of argon gave deflections which were 10 mm less than those found at 30 ml/min of argon within the range 0·1–1·0 ml at S.T.P.

4. *Voltage*: Deflections for detection at 1750 v were about half those at 2000 v.

Provided that calibrations are repeated at regular intervals, that air is excluded from the column, and that the column is regularly baked to remove impurities, that temperature is maintained constant (say 20 $\pm$ 2°) and that flow rate is maintained constant (say 30 $\pm$ 2 ml/min), the argon chromatograph is capable of giving a quantitative measure of hydrogen, accurate to $\pm 5\%$.

Methane

Methane gave a positive deflection, very much smaller than that found for an equal

volume of a higher hydrocarbon. The most satisfactory parameter of the response peak to use in quantitative analysis differed with the concentration range. At low concentrations, 0·01–0·10 ml at S.T.P., maximum peak height was found to be very nearly directly proportional to the volume admitted; there was a *very slight* curve in the same sense as in Fig. 2. This peak height was slightly affected by argon flow rate, but both the curvature of the calibration graph and the sensitivity increased with temperature (the peak height for 0·05 ml at S.T.P. of methane was 34 mm at 20° and 52 mm at 38°).

At concentrations >0·1 ml at S.T.P. the peak first broadened, then showed pronounced inversion. Here the most satisfactory parameter for use in quantitative work was peak "area", found by adding (*i*) the small initial negative kick (*a*), (*ii*) the maximum positive deflection (*b*), and (*iii*) the distance of the maximum inverted distance below height *b* (*c*), and multiplying by the peak width (*w*) measured at $\frac{1}{2}(a + b + c)$ (*i.e.*, assuming that the peak has been formed by a "folding over" process). Such "areas" were directly proportional to the volume of methane injected but were very sensitive to:

1. *Temperature:* The height at which peak inversion occurred (*b* above) was very sensitive to temperature. A calibration plot of "areas", with column and detector at 37°, was almost parallel to a similar plot at 20°, but was displaced to the equivalent of 0·15 ml at S.T.P., which, in estimating volumes in the range 0·20–1·0 ml at S.T.P., represents a very large error.

2. *Argon flow rate:* Reduction of argon flow rate from 30 to 18 ml/min, under otherwise identical conditions, resulted in such a large increase in *w* that the apparent peak "area" for a given dose was almost doubled.

3. *Detector voltage:* Reduction of detector voltage 2000 to 1750 v caused the value of *b* to be halved and the apparent peak "areas" were almost halved.

From a series of calibrations made at intervals over 12 months it was found that reliable, reproducible calibrations could be obtained, provided that detector temperature and argon flow rate were both standardised. Calibrations for methane were found to be slightly more sensitive to these variables than the corresponding results for hydrogen, but, with care, it was found possible to achieve an estimated accuracy of ±5%. In cracking studies, where methane was virtually the only product, volumes estimated by the above technique agreed, to within about 7%, with those calculated from volumetric measurement of the quantity of hydrocarbon cracked.

Preliminary work using cylinder helium in place of argon as the carrier gas showed that the response to methane was similar in magnitude to that found in an argon stream.

Carbon dioxide

Carbon dioxide was determined after elution from the column thermostatted at 100° by the jacket in the instrument as supplied. A negative deflection was found; typical response peaks are sketched in Fig. 3. Each peak could be divided into three parts: (*i*) an initial "kick", (*ii*) a peak with a well defined maximum which depended on the volume of carbon dioxide injected, and (*iii*) a second, broader maximum the height of which did not vary appreciably with the volume of gas injected. Two parameters of response peaks were found suitable for determinations:

(*a*) the height of peak (*ii*), measured using the top of peak (*iii*) as the zero peak height; *x* in Fig. 3 where *x* is positive for large volumes of carbon dioxide (A) and

negative for smaller volumes (B). A linear relation was found between x and the volume of carbon dioxide injected in the range 0·15–1·0 ml at S.T.P. It was not, however, found practicable to measure volumes of carbon dioxide less than 0·15 ml at S.T.P. by this method.

(*b*) peak "area" measured by maximum peak height above the base line, y, multiplied by peak width at $y/2$. The latter calibration was more satisfactory in the determination of volumes greater than 1·0 ml at S.T.P., and a linear relation was found between "area" and volume of gas injected.

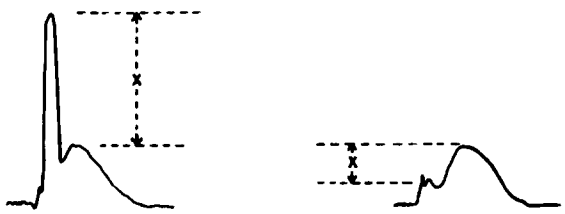


FIG. 3.—Detector response shape for carbon dioxide. Dose A was larger than dose B.

The carbon dioxide response peak was sensitive to the presence of impurities; for example peak shape was altered when sulphur dioxide was being eluted from the column simultaneously. Provided that conditions are controlled, and that care is taken to exclude impurities such as sulphur dioxide, determinations could be made with an estimated accuracy of $\pm 5\%$.

Carbon monoxide

Carbon monoxide, detected on elution from the column at 100°, gave a sharp negative peak, similar in appearance to that of hydrogen; but the calibration plot of peak height against volume injected was very much more curved than in Fig. 2. At volumes greater than 0·4 ml at S.T.P. the plot became so flat that this parameter could no longer be regarded as satisfactory for use in quantitative work. Calibrations made with a 5-month interval, in the range 0–0·4 ml at S.T.P., using the column at 100°, and a flow of 25 ± 1 ml/min of argon, were coincident. It is concluded from these results that the instrument can be used for the determination of carbon monoxide with about the same degree of accuracy as that of hydrogen, provided that the same accuracy of control of operating conditions is observed.

A study of the effect of impurities on the deflection given by carbon monoxide showed (*i*) that simultaneous elution of small traces of ammonia from the column increased the apparent deflection. In one example studied, the calibration plot was apparently increased by about 40 mm throughout most of its length by a very small amount of ammonia which was simultaneously eluted; and (*ii*) that a carbon monoxide peak, eluted while a sulphur dioxide peak was being simultaneously eluted, had a maximum peak height the same distance above the extrapolated zero deflection line as would have been expected in the absence of the sulphur dioxide peak. The sulphur dioxide trace merely rendered invisible the lower portion of the peak. Small amounts of carbon monoxide could not be determined while sulphur dioxide was being eluted.

Nitrogen

A single calibration for nitrogen showed that it gave a negative peak identical in shape with that given by cabon monoxide; and the calibration plot for nitrogen detected at 20° was almost coincident with that of carbon monoxide at 23° except that the deflection for the former was marginally lower than that of the latter in the flattened region (more than 0·4 ml at S.T.P.).

Sulphur dioxide

When eluted from the charcoal column at 100°, sulphur dioxide gave a large negative peak with a long tail. A plot of maximum peak height against volume of gas injected showed an initial steep rise (0–0·2 ml at S.T.P.) followed by a decreasing rate of increase of peak height with increase in volume injected (0·2–1·0 ml at S.T.P.). This calibration was only acceptable for a dose which was eluted *after* the recorder had returned to its original zero reading; any overlap of peaks vitiated the calibrations.

Ethane, propane and n-pentane

All three compounds showed a positive response, and plots of peak "area" (height × width at half height) against volume of gas injected were, within experimental error, linear over the range 0–0·003 ml at S.T.P. The instrument is very much more sensitive to these compounds than to the substances discussed earlier, and the calibration plots showed scatter arising from difficulties in handling and measuring small doses of gas. Results, expressed as the mean "area" of response peaks (mm²) for samples of 0·001 ml at S.T.P. of gas for calibrations over a range of detector voltages are summarised in Fig. 4.

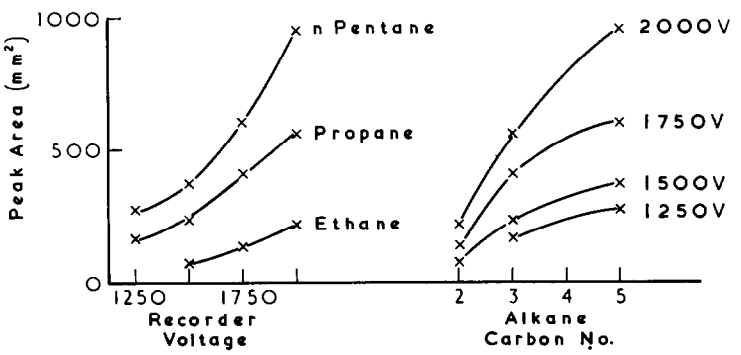


FIG. 4.—Plot of peak "areas" (see text for definition) against detector voltage for 0·001 ml at S.T.P. for ethane, for propane and for n-pentane.

Oxygen

Attempts to use the instrument for the determination of oxygen were unsuccessful. A large negative peak was observed, but conditions for quantitative work were not established.

Ammonia

Large positive peaks were observed which had a long tail. As noted earlier (see *Carbon monoxide*), traces of ammonia can make analyses of permanent gases unreliable.

Hydrogen sulphide

Large positive peaks arising from hydrogen sulphide were observed during analysis of hydrogen sulphide-hydrocarbon mixtures when a dinonylphthalate supported on a "Celite" column was used as the stationary phase. Small traces of hydrogen sulphide eluted simultaneously with hydrocarbons apparently increased the hydrocarbon response peak height. Quantitative investigations of this effect were not made but it was clear that sensitivity to hydrocarbons was increased by the presence of traces of hydrogen sulphide.

DISCUSSION

The ionisation potentials of the substance discussed above, listed in volts in decreasing order of magnitude, are:[8]

Hydrogen	15·6	Nitrogen	15·51
Methane	14·5	Carbon dioxide	14·4
Carbon monoxide	14·1	Sulphur dioxide	13·1
Ethane	12·8	Oxygen	12·5
Metastable argon[2]	11·7		
Ammonia	11·2	Hydrogen sulphide	10·42

Any quantitative theory for the detector response characteristics cannot be directly based on the values of ionisation potential alone, since both the shape of the peak and the calibration plots for hydrogen, nitrogen and carbon monoxide were similar, but differed from those of methane and carbon dioxide, which have ionisation potentials between those of nitrogen and carbon monoxide; and, furthermore, the characteristics of methane and carbon dioxide did not resemble each other. The quantitative response of the detector may be expected to be dependent on (*i*) the ionisation potential of the compound and the average life-time of the excited species, (*ii*) the concentrations and nature of all impurities in the detector at the same time (specific examples have been noted above when the effect of various impurities on individual gases were discussed), and (*iii*) the variation, with time, of concentration of material as it is eluted from the column (this accounts for the marked "tailing" of the sulphur dioxide peak). The complexity of these factors make quantitative calculations difficult, but it may be noted that most of those substances which have ionisation potentials greater than 11·7 v produce negative peaks, showing that they cause a fall in the standing current of the detector.

Negative peaks were found to give adequate accuracy for use in quantitative analysis provided that the concentration of impurities (*e.g.*, air) was carefully controlled, the temperature of the column and detector were maintained constant (say $\pm 2°$) and the flow rate was constant (say 30 ± 2 ml/min). Those compounds for which peak width was used as a response parameter were very sensitive to flow rate. All peaks were sensitive to detector temperature; McWilliam,[9] quoting results of Lovelock, James and Piper,[10] has noted that the absolute sensitivity of the argon detector is very dependent on temperature. The results of the present work show that the determination of hydrogen, methane, nitrogen, carbon monoxide and carbon dioxide may be made with an estimated accuracy of about 5% provided that the conditions stated are observed. To produce an increase in accuracy, more accurate control of the detector temperature would be necessary.

The sensitivity of the instrument to the ethane-pentane series is seen (Fig. 4) to increase markedly with detector voltage (also noted for hydrogen and methane) and

with chain length; the latter effect is readily explained by the ionisation potentials of the compounds. Although the ionisation potentials of both methane and ethane are greater than that of argon, a positive response is found, but this is very much less than for the higher hydrocarbons, in agreement with the data of Lovelock.[2]

Since the responses obtained in the present study may result from or may be sensitive to the presence of impurities in the argon supply it is necessary to repeat calibrations for each substance with each new argon cylinder used. In the author's experience, however, calibration curves for the determination of hydrogen and methane were constant, within experimental error, for several different argon cylinders.

Application of the argon chromatograph to kinetic studies

The almost complete absence of disturbance peaks when a sample is injected, and the rapid re-establishment of equilibrium conditions in the detector after interruption of the argon flow, made the apparatus useful for studying the kinetics of reactions involving permanent gases, where it is desirable to make frequent analyses of the products (*e.g.*, ref. 11). Using the apparatus under conditions described above, with the charcoal column held at 22°, it was possible to analyse one sample of a hydrogen-methane mixture every 6 min. The only other product in the particular reaction studied was ethane, which had a retention time of some 2·5 hr. The effect of this on subsequent analyses could be eliminated by removing the column from its jacket and heating (while the flow of argon was maintained) with a bunsen flame so that a hot zone moved slowly from the top to bottom of the column; the column was cooled in the argon flow and reconnected to the detector, and after some 10 min hydrogen-methane analyses were resumed. The same column, held at 100°, could be used to follow kinetics of the ethane formation reaction if samples were withdrawn at accurately controlled intervals (see ref. 11).

A similar technique was used to study the dissociation of ammonia on a solid catalyst, the column being removed and heated just before the expected time of elution of the ammonia peak. Repeated heating of the column was necessary here, however, to ensure complete removal of ammonia, traces of which vitiated the detector response calibrations for hydrogen and nitrogen.

Retention times on the charcoal column were such that quantitative analyses of the following product mixtures could be made at approximately 10-min intervals by selection of appropriate length of column, operating temperature and argon flow rate: hydrogen-carbon monoxide-carbon dioxide-methane; hydrogen-nitrogen-methane; methane-ethane. Calibrations must be repeated under each new set of operating conditions.

Corrosive gases

The potential radioactive hazard which could result from damage to the detector by corrosive gases in mixtures to be analysed makes it necessary to remove any corrosive material before it enters the radioactive chamber. In a particular study where the products of the reaction to be studied consisted of ethane and higher hydrocarbons in addition to appreciable quantities of hydrogen chloride, the author found that the corrosive products could be removed by passing the gas to be analysed through a bed (20×2 cm) of sodium hydroxide pellets after the injection of the gas into the argon stream, but before it passed through the column. This procedure invariably increased

the width of the peak. No peaks attributed to hydrogen chloride were found on the chromatograph trace and it was concluded that this gas was quantitatively removed by the alkali. Hydrogen sulphide could be removed similarly, but it was necessary to replace the alkali with fresh material frequently, since traces of hydrogensulphide were detected in the effluent gases some 30–40 min after the sample was injected when analyses were made using a dinonylphthalate column (120 cm long). Elution of traces of hydrogen sulphide was shown by a slight positive rise in the base line, accompanied by a marked rise in sensitivity of the apparatus for the detection of hydrocarbon. It was found that the sodium hydroxide could be changed quickly with little influence on the identification of substances having comparatively large retention distances but quantitative studies would undoubtedly be subject to very considerable errors.

A single detector containing radium-D was used throughout all the work reported in the present paper. It gave excellent service for some two years, during which it was operated at 2000 v and was frequently heated for short periods to 200°. Subsequently some 100–200 doses (of around 0·8 ml at S.T.P.) of each of the corrosive gases hydrogen sulphide, water vapour and sulphur dioxide were passed through it at 20–100°. This treatment is more severe than the apparatus may be reasonably expected to withstand, but no appreciable radiation, above the background, was found on routine monitoring of the detector, though internal examination finally showed that corrosion had started, and the makers recommended that the detector should be replaced. On fitting a new 20-millicurie ^{90}Sr source to the instrument, there was an appreciable rise in the radiation detected outside the case, and additional shielding was fitted around the outside of the detector case.

Acknowledgements—The author would like to thank Dr. P. W. Darby and Mr. F. Shephard for helpful comments on the manuscript of this paper, and Dr. R. J. Magee of the Chemistry Department, The Queen's University of Belfast, for monitoring the radioactivity of the apparatus.

Zusammenfassung—Es wurde gefunden, dass die chromatographische Bestimmung von Wasserstoff, Methan, Kohlenmonoxyd, Kohlendioxyd und Stickstoff im Bereich 0·1–1·0 ml (Normalbedingungen) mit einer Genauigkeit von etwa 5% möglich ist. Ein radioaktiver Ionisationsdetector wurde verwendet und die Strömungsgeschwindigkeit des Trägergases wurde innerhalb bestimmter Grenzen konstant gehalten. Ergebnisse über die Untersuchung der Empfindlichkeit des Instrumentes gegenüber Sauerstoff, Schwefeldioxyd, Äthan, Propan und n-Pentan werden ebenfalls mitgeteilt. Besonderes Augenmaek wurde darauf gerichtet die bestgeeigneten Parameter fur das Kurvenmaximum bei quantitaiven Bestimmungen festzulegen. Einige besondere Anwendungsmöglichkeiten des Argon-Chromatographen bei kinetischen Studien mit permanenten Gasen, sowie eine Methodezur Entfernung korrodierender Gase von Analysengemischen werden behandelt.

Résumé—L'auteur montre qu'il est possible de mesurer quantitativement des volumes d'hydrogène, de méthane, d'oxyde de carbone, de gaz carbonique et d'azote compris entre 0,1 et 1,0 ml dans les conditions normales de température et de pression, avec une précision de 5 pour 100 en utilisant un chromatographe en phase gazeuse muni d'un détecteur à ionisation dans la mesure où la température du détecteur et la vitesse du gaz porteur à travers la colonne sont maintenus dans des limites déterminées. Les résultats d'essais de détermination de la sensibilité de l'instrument pour l'oxygène, le gaz sulfureux, l'éthane, le propane et le n-pentane sont également donnés. L'auteur s'est particulièrement attaché à déterminer le paramètre le plus commode

permettant d'agir sur les pics en vue de la mise au point d'analyses quantitatives. Quelques applications particulières du chromatographe à l'argon dans les études de cinétique chimique sont décrites et une méthode permettant l'élimination de gaz corrosifs dans les mélanges à analyser est discutée.

REFERENCES

[1] J. E. Lovelock, *J. Chromatog.*, 1958, **1**, 35.
[2] *Idem, Third International Symposium on Gas Chromatography, Edinburgh*, 1960. Butterworths, London.
[3] V. Willis, *Nature*, 1959, **184**, 894.
[4] R. Berry, *ibid.*, 1961, **188**, 578.
[5] *Idem, ibid.*, 1961, **190**, 1187.
[6] W. A. Wiseman, *ibid.*, 1961, **190**, 1187.
[7] A. K. Galwey, *Chem. and Ind.*, 1960, 1417.
[8] *Handbook of Chemistry and Physics.* Chemical Rubber Publishing Co., Cleveland, 41st Ed. Pp. 2549–51.
[9] I. G. McWilliam, *Rev. Pure and App. Chem.*, 1961, **11**, 33.
[10] J. E. Lovelock, A. T. Jones and E. A. Piper, *Ann. N.Y. Acad. Sci.*, 1959, **72**, 720.
[11] A. K. Galwey, *J. Catalysis*, 1962, **1**, 227.

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SHORT COMMUNICATIONS

Contributions to the basic problems of complexometry—X:* Determination of nickel and cobalt in the presence of iron, copper and some other metals

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THE problem of successive determination of nickel and cobalt in the same solution has not yet been satisfactorily solved, especially in the presence of iron, copper and other elements, which need to be considered in the analysis of alloys. A few years ago[1] a procedure utilising the high stability of the cobalt^{III}-EDTA complex (pK 40·7) was proposed.[2] The complex of tervalent cobalt with EDTA is formed very easily in an alkaline medium by hydrogen peroxide oxidation and Schwarzenbach[3] ascribes to it the composition $Co(OH)Y^{2-}$. The original determination of nickel and cobalt was based on the different reactivity of $Co(OH)Y^{2-}$ and NiY^{2-} complexes with potassium cyanide. The former does not react, while the latter quantitatively forms a nickel-cyanide complex. The sum of nickel and cobalt can be determined indirectly by adding an excess of EDTA in an ammoniacal medium, then titrating the excess of EDTA with magnesium chloride using Eriochrome Black T as indicator. After the oxidation of cobalt with hydrogen peroxide and screening nickel with potassium cyanide, a second titration is carried out with magnesium chloride to determine the EDTA liberated from the NiY^{2-} complex.

The complex $Co(OH)Y^{2-}$ is coloured intensely blue so that this procedure can be used only for amounts of cobalt not exceeding 10 mg in 100–150 ml of solution to be titrated. Iron must not be present and it cannot be screened with triethanolamine (TEA) because of the reaction of the Fe-TEA complex with the indicator. Other elements also interfere.

In an acidic medium there also exists a ruby red complex, $Co(H_2O)Y^-$ or CoY^-. Indirect determination of cobalt is then possible even in a relatively acidic medium where many elements do not interfere. Kinnunen and Wennestrand[4] use a back-titration of added excess EDTA with thorium nitrate and Xylenol Orange as indicator. Flaschka and Ganchoff[5] titrate the added excess EDTA with bismuth and follow the titration photometrically using Pyrocatechol Violet as indicator. Neither of these methods makes possible the determination of cobalt in the presence of iron. Their practical application is therefore very limited.

In solving the given problem a return was made to the original method of determination of nickel and cobalt in an alkaline medium, elaborated in 1953, when only Eriochrome Black T was known as a complexometric indicator. Today there are other very suitable indicators for a strongly alkaline medium *e.g.* Thymolftalexon or Fluorexon (Calcein). In a solution of potassium hydroxide (pH 12) traces of calcium give with Fluorexon a very intense green fluorescence which is easily discernible even in the presence of the highly coloured cobalt complex CoY^-. The strongly alkaline medium also permits the masking of iron as a colourless TEA complex. Further, it has been found that thioglycollic acid (TGA), which does not react with the nickel- and cobalt-EDTA complexes, masks other elements which may be present, *e.g.* copper, lead, bismuth, zinc, *etc.* Under these conditions the new method becomes highly selective for cobalt and nickel.

EXPERIMENTAL

Reagents

0·05*M* EDTA solution and 0·05*M* solutions of cobalt and nickel nitrates, copper sulphate, iron^{III} chloride and lead nitrate were prepared from reagent grade chemicals and their strengths controlled by complexometric titrations.

Fluorexon (CHEMAPOL, Prague, Czechoslovakia) diluted with potassium nitrate (1:100), 0·5% Xylenol Orange (Chemapol), 1*M* potassium hydroxide, 20% triethanolamine, 15% thioglycollic acid (Merck, Darmstadt, Germany), 20% thiourea, solid potassium cyanide and urotropine.

* Part IX: *Talanta*, 1962, **9**, 23.

Determination of the sum of nickel and cobalt

Although the solutions of nickel- and cobalt-EDTA complexes are coloured, the indirect determination of both elements is possible in three different ways:
(a) By back-titration with lead nitrate at pH 5–5·5 to a Xylenol Orange end-point.
(b) By back-titration with a calcium salt at pH 10–11 to a Thymolftalexon end-point.
(c) By back-titration with a calcium salt at pH 12–13 to a Fluorexon end-point.

All of these colour changes are very sharp at the end-point, even at high concentrations of both elements. With Xylenol Orange it is possible to determine 50 mg of cobalt or nickel in 100 ml of titrated solution and with the other two methods the maximal permitted concentration of both elements is about the same. The first method has the advantage that the alkaline earth elements do not interfere if masked by fluoride. In the second method iron and aluminium do not interfere if screened with TEA. A combination of methods (a) and (c) is more suitable for practical application if one expects the presence of other elements.

Procedure. (a) To a slightly acid solution add a small excess of 0·05*M* EDTA and a few drops of Xylenol Orange. Add solid urotropine to adjust the pH to 5–5·5, then titrate with 0·05*M* lead nitrate solution to an intense red-violet coloration.

Procedure. (c) To a slightly acid solution add a small excess of EDTA and 1*M* KoH to its final concentration 0·1*M* (after suitable dilution). After addition of Fluorexon titrate the solution with calcium salt to the appearance of a vivid yellow-green fluorescence. Titration in diffuse day light is recommended.

Determination of nickel in presence of cobalt

As has been already stated, the cobalt^{III}-EDTA complex is inactive against potassium cyanide, while the nickel-EDTA complex reacts quantitatively. The determination of nickel can be carried out in one of two ways.

After determination of the sum of nickel and cobalt according to *Procedure* (*c*), add 1–5 ml of 3% hydrogen peroxide, mix thoroughly and set aside for 5 min. The solution becomes coloured blue, then add 0·2–0·5 g of potassium cyanide and after 5–10 min titrate the liberated EDTA with a calcium salt to a green fluorescence, which is very clearly visible at the edge of the surface in strongly coloured solutions. Alternatively, oxidise cobalt first, as described, titrate the excess of EDTA with calcium, and after addition of potassium cyanide titrate once more. In this simple way we determine both nickel and cobalt.

Determination of nickel and cobalt in the presence of iron

In a strongly alkaline medium tervalent iron forms a colourless complex with TEA even in the presence of EDTA. The addition of EDTA on the contrary is useful here, because these solutions are free of colloidal iron hydroxide.[7]

Procedure. To the acid solution of iron, cobalt and nickel, add a sufficient amount of EDTA, 20 ml of 20% triethanolamine solution, and 1*M* potassium hydroxide to a final concentration of 0·1*M*. The sum of nickel and cobalt is determined by back-titration with a calcium salt. This titration can be carried out with hydrogen peroxide before or after oxidation. For screening nickel, potassium cyanide must be added after the addition of peroxide.

Determination of nickel and cobalt in the presence of copper

The determination of the sum of nickel and cobalt, then of copper presents no difficulties as recently described.[6] It is based on the sum of all three elements by back-titration with calcium and on the masking of copper with TGA in the same solution. If we wish to determine cobalt besides nickel, we must oxidise cobalt with hydrogen peroxide before the addition of TGA. In its presence the oxidation of cobalt is not quantitative, but once the complex $Co(OH)Y^{2-}$ is formed it is not reduced with TGA at all or only very slowly.

Procedure. To the slightly acid solution add an excess of EDTA, potassium hydroxide and hydrogen peroxide as described above. After oxidation (5 min) add 5–10 ml of a neutralised solution of 15% thioglycollic acid and titrate with calcium salt using Fluorexon as indicator. After addition of potassium cyanide, determine nickel.

Determination of nickel and cobalt in the presence of iron and copper

The procedure described below is actually a combination of the two foregoing procedures. It has to be emphasised that copper forms very stable complexes with EDTA as well as with TEA, so that its determination in an alkaline medium is impossible. It is, however, possible to mask copper with TGA and it is known that TGA forms intense red complexes with iron in an alkaline medium. The presence of TEA and potassium hydroxide prevents the latter reaction.

Procedure. To the solution containing all four elements add an excess of EDTA, 20 ml of 20% triethanolamine, enough 1*M* potassium hydroxide, 1–5 ml of 3% hydrogen peroxide and after 5 min 5–10 ml of neutralised 15% thioglycollic acid. By back-titration with calcium salt the sum of cobalt and nickel is obtained. After addition of 0·2–0·5 g of potassium cyanide, continue the titration with calcium salt (determination of nickel).

The above method gives good results. All colour changes at the end-point are sharp, but are unfavourably influenced by high concentrations of ammonium and sodium salts.[6] The complex $Co(OH)Y^{2-}$ is very stable, but tends to react with TGA and with potassium cyanide (reduction and complex formation). This unfavourable influence is observed only 30 min after the end of the titration and is therefore without practical value.

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Summary—A complexometric determination of nickel and cobalt in the same solution has been devised. It is based on the determination of the sum of nickel and cobalt by back-titration of added excess EDTA in a strongly alkaline medium with calcium chloride using Fluorexon (Calcein) as indicator. After oxidation of cobalt with hydrogen peroxide to form the cobalt^{III}- EDTA complex and screening of nickel by potassium cyanide, the liberated EDTA corresponding to the amount of nickel present is titrated with further calcium chloride. High concentrations of iron and aluminium are screened with triethanolamine. Copper and other heavy metals are screened with thioglycollic acid.

Zusammenfassung—Die komplexometrische Bestimmung von Kobalt und Nickel in derselbeu Lösung wird beschrieben. Zuerst wird die Summe Co + Ni in alkalischem Medium ermittelt, indem der Ueberschuss von ÄDTE mit Calciumchloridlösung gegen Fluorexon-(Calcein)-Indicator zurücktitriert wird. Nach Oxydation des Kobalts zum dreiwertigen Komplex mittels Wasserstoffperoxyd wird Nickel durch Zusatz von Kaliumcyanid maskiert und die freiwerdende Menge ÄDTE mit Calcium titriert. Selbst grosse Mengen von Eisen und Aluminium können mit Triäthanolamin maskiert werden. Kupfer und andere Schwermetalle werden mit Thioglykolsäure ausgeschaltet.

Résumé—Les auteurs ont mis au point le dosage complexométrique du nickel et du cobalt présents dans la même solution. Il est fondé sur la détermination de la somme du nickel et du cobalt par titrage en retour de l'E.D.T.A. en milieu fortement alcalin par le chlorure de calcium en présence de calcéine comme indicateur. Après oxydation du cobalt en complexe EDTA-Co(III) par l'eau oxygénée, le nickel est complexé par le cyanure de potassium; l'E.D.T.A. libéré, qui correspond au nickel présent est titré à nouveau par le chlorure de calcium. Le fer et l'aluminium même présents en grandes quantités, sont complexés par la triéthanolamine. Le cuivre et les autres métaux lourds sont complexés par l'acide thioglycolique.

REFERENCES

[1] R. Přibil, *Chem. Listy*, 1954, **48**, 825: *Coll. Czech. Chem. Comm.*, 1954, **19**, 1171.
[2] C. N. Reilley, W. G. Scribner and C. Temple, *Analyt. Chem.*, 1956, **28**, 450.
[3] G. Schwarzenbach, *Helv. Chim. Acta*, 1949, **32**, 839.
[4] J. Kinnunen and B. Wennestrand, *Chemist-Analyst*, 1957, **46**, 92.
[5] H. Flashka and I. Ganchoff, *Talanta*, 1961, **8**, 885.
[6] J. H. Eggers, *ibid.*, 1960, **4**, 38.
[7] R. Přibil, J. Körbl, B. Kysil, J. Vobora, *Coll. Czech. Chem. Comm.*, 1959, **24**, 1799.

Beobachtungen am Verbrennungsverlauf organischer Substanzen

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BEI der Durchführung von Kohlenstoff—und Schwefelbestimmungen nach der relativkonduktometrischen Methode, wie sie bereits des öfteren beschrieben wurde,[1–5] ergeben sich weitere auswertbare Möglichkeiten dieser neuen Arbeitstechnik, die im folgenden in Kürze ihrem Wesen nach aufgezeigt werden sollen.

Die relativkonduktometrische Methode beruht auf der Leitfähigkeitsdifferenzmessung in zwei

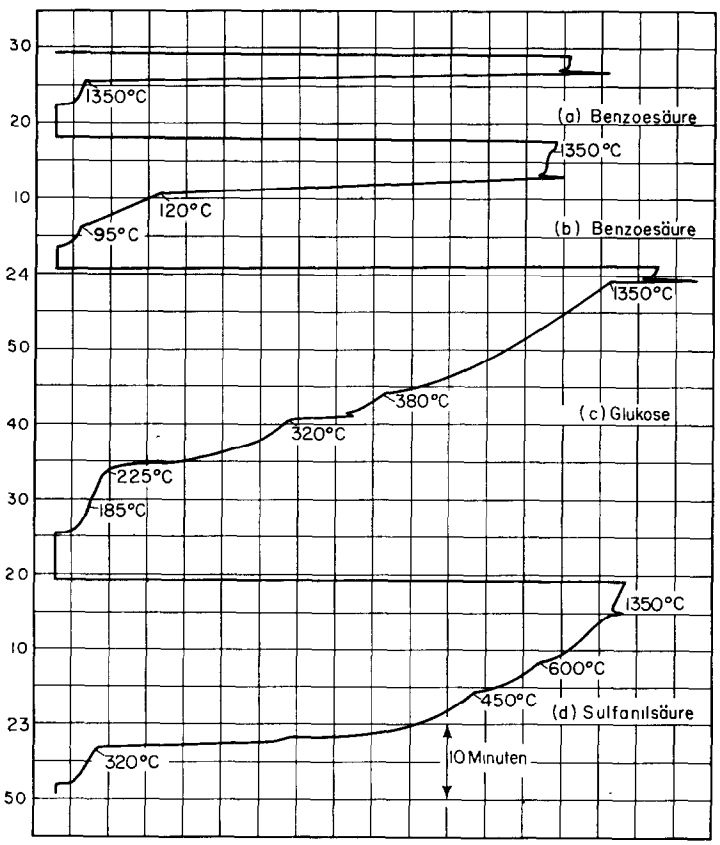


ABB. 1.—Registrierung von Kohlenstoff-Bestimmungen in einigen Einwaagen organischer Substanzen.

Zellen, die eine gefüllt mit unbegaster, die andere gefüllt mit der mit CO_2 oder SO_2 begasten Absorptionslösung. Die Aufzeichnung dieser Leitfähigkeitsdifferenzen erfolgt mittels automatisch registrierendem Schreiber, der ein Integral über das während einer Verbrennung auftretende Gas bzw. die durch dessen Absorption in geeigneten Lösungsmitteln verursachte Leitfähigkeitsdifferenz liefert. Das heißt somit, diese integrierende Aufzeichnung findet auf jeden Fall statt, ob nun die Verbrennung rasch oder langsam erfolgt, wobei unter "rasch" eine Zeitdauer von weniger als 1/2 Minute, unter "langsam" eine von 1/2 Minute bis zu einer Stunde und mehr verstanden wird.

Es liegt im Interesse des Analytikers, die Verbrennung rasch durchzuführen, erstens, weil die Resultate bei explosionsartig verlaufenden Verbrennungen infolge der eindeutigeren Aufzeichnung durch den Schreiber weniger streuen und zweitens, weil die Stärke dieser Methode vor allem in der kurzen Dauer einer einzelnen Bestimmung liegt.

Nun scheint aber ein weiterer großer Vorteil dieser Methode darin zu bestehen, daß man—ohne Rücksicht auf die Zeitfrage—bei sogenannten "gelenkten Verbrennungen" fraktionierte und temperaturkontrollierte Verbrennungsabläufe auch mit sehr geringen Substanzmengen (etwa 1 mg) studieren kann. Wird nämlich die zu verbrennende Probe nicht plötzlich von 20°C auf 1350°C

gebracht, sondern durch langsames Einschieben mit geeigneten Vorrichtungen dieser Temperaturbereich in 1, 2, 10, 20 Minuten oder beliebig länger durchlaufen, so erhält man an Stelle einer waagrechten Linie eine in mehreren Stufen bzw. Kurven aufsteigende Aufzeichnung auf dem Registrierstreifen, die bei Einhaltung der gleichen Versuchsbedingungen für die einzelnen Substanzen reproduzierbar ist und die möglicherweise Kohlenstoff-bzw. Schwefelanteilen mit bestimmten Bindungscharakter in der Substanz entspricht.

An Hand von einigen Beispielen von Verbrennungen und ihren Aufzeichnungen durch den Schreiber möge das Gesagte veranschaulicht werden. Siehe dazu Abb. 1: Registrierung des Kohlenstoff-Gehaltes einiger Einwaagen verschiedener organischer Substanzen.

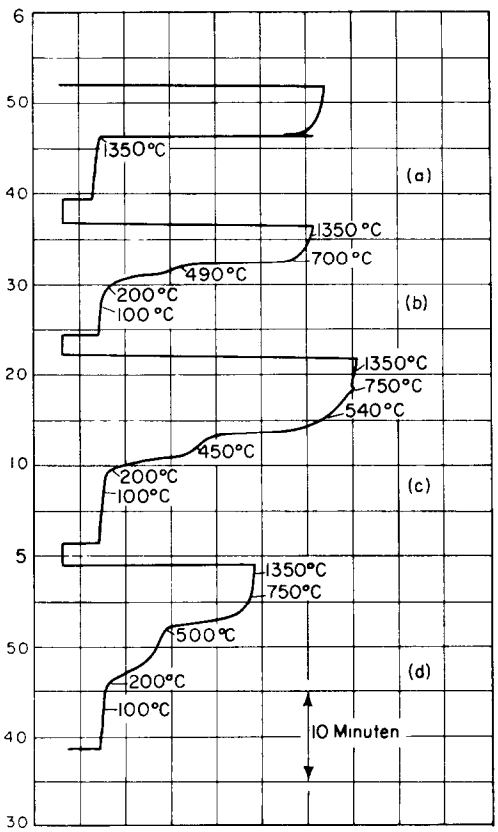


ABB. 2.—Registrierung von Schwefel-Bestimmungen in einigen Einwaagen eines schweren Heizöles (3,6% S).

Die erste Aufzeichnung zeigt den Verbrennungsablauf von Benzoesäure unter den üblichen Bedingungen (Abb. 1a), d.h. rasches Einschieben der Probe in den auf 1350°C erhitzten Verbrennungsofen. Die Verbrennung und Registrierung erfolgt in diesem Fall unter Berücksichtigung einer Überkonzentrationsspitze in max. 2 Minuten.

Die zweite Aufzeichnung (Abb. 1b) zeigt die Verbrennung der gleichen Substanz, wobei aber das Einschieben in den Ofen stufenweise erfolgt. Man kann auf diese Weise eine ungefähre Zersetzungstemperatur der Substanz ermitteln und weiters eine stufenweise Verbrennung durchführen, wobei in jeder durchschrittenen Temperaturstufe ein gewisser Prozentsatz des Kohlenstoff-Gehaltes der Substanz in CO_2 übergeht. Der Aufzeichnung entnimmt man, daß unter den gegebenen Bedingungen die Zersetzung der Benzoesäure bei 95°C einsetzt, bei 120°C zu 95% verlaufen ist und beim Einschieben auf 1350°C nur mehr ein kleiner Restbetrag an Kohlenstoff registriert wird. Das Verhältnis des Kohlenstoffes in der COOH-Gruppe zum Kohlenstoff im Ring, ist 1:6. Die auf die waagrechte projizierten, den freiwerdenden Kohlenstoffmengen entsprechenden Strecken 95–120°C und 120–1350°C verhalten sich ebenfalls etwa wie 1:6. Inwieweit es sich hier um einen Effekt, welcher durch den Verdampfungs-bzw. Zersetzungsbeginn der betreffenden Substanz hervorgerufen wird bzw. um echte Unterschiede im C-Bindungscharakter, müßte noch geklärt werden.

Die dritte Aufzeichnung (Abb. 1c) gibt den Verbrennungsverlauf von Glukose wieder. In diesem Fall beginnt die Zersetzung erst bei 185°C, ist bei 225°C zu 35%, bei 320°C zu 50% und bei 1350°C zu 100% vor sich gegangen. Eine Interpretation der Stufenbildung muß genaueren Untersuchungen vorbehalten bleiben.

Die vierte Aufzeichnung (Abb. 1d) zeigt die Verbrennung von Sulfanilsäure. Der Zersetzungsbeginn liegt in diesem Fall erst bei 320°C, bei welcher Temperatur ca. 75% des Gesamt-Kohlenstoffes freigemacht werden. Die restlichen 25% werden stufenweise bis zu einer Endtemperatur von 600°C erfaßt,

Entsprechendes dazu läßt sich auch bei Schwefelbestimmungen feststellen.

Versuche, bei denen Sulfonal verwendet wurde, zeigen beispielsweise, daß bei Einschieben einer Einwaage in den kalten Ofen und langsamen Anheizen auf 1350°C nur 4,27% der zu erwartenden Schwefel-Menge vom Schreiber registriert wurden, während der Großteil der Probe weit unter der Siedetemperatur vergaste und vom Sauerstoffstrom weggeführt wurde, ohne in SO_2 übergeführt worden zu sein.

Bei einem weiteren Versuch, durchgeführt in einem auf 600°C erhitzten Verbrennungsrohr, konnten auch nur 8,70% des Schwefelwertes erfaßt werden. Auch bei dieser Temperatur scheint die Geschwindigkeit der Verbrennung noch zu klein zu sein, um zu verhindern, daß unzersetzte Substanzmengen vom Sauerstoff-Strom aus der heißen Zone weggeführt werden, noch bevor sie zu SO_2 umgesetzt werden konnten.

Erst Versuche, die bei einer Ofentemperatur von 1350°C durchgeführt wurden, ergaben je nach Versuchsbedingungen eine 95–100% ige Registrierung der zu erwartenden Schwefel-Mengen.

An Hand von Verbrennungen von Erdölprodukten, durchgeführt durch langsames Einschieben der Proben in den heißen Ofen (im Verlauf von 5–20 Minuten und mehr) kann analog zu den Kohlenstoff-Bestimmungen gezeigt werden, daß man auch damit differenzierte Verbrennungen erhält. Bild 2 zeigt Registrierungen von Schwefel-Bestimmungen in einigen Einwaagen von einem schweren Heizöl.

Die Aufzeichnungen a und b (Einschieben einer Einwaage im Verlauf von 1 bzw. 5 Minuten) zeigen noch keine Differenzierung in verschieden flüchtige Anteile. Erst bei einer Einschiebedauer von 10 bzw. 20 Minuten (Aufzeichnung c und d) treten stufenweise Registrierungen auf. Zwischen Raumtemperatur und 200°C scheinen dabei keine wesentlichen Anteile an flüchtigen Schwefelverbindungen zu verbrennen. Im Temperaturbereich von 200–500°C vergasen bzw. verbrennen Produkte, die etwas mehr als 35% des Gesamtschwefels enthalten und der Rest wird zwischen 500–750°C in SO_2 übergeführt. Über dieser Temperatur bis 1350°C waren keine schwefelhaltigen Verbindungen mehr zu erfassen.

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LITERATUR

[1] W. Koch, S. Eckhard und H. Malissa, *Arch. Eisenhütt.*, 1958, **29**, 543.
[2] H. Malissa, *Microchim. Acta*, 1957, 553.
[3] *Idem, ibid.*, 1960, 127.
[4] W. Schmidts und W. Baasch, *Forschungsber. Wirtsch. und Verkehrsmin. NRW*, Nr. 67, 1954. Westd. Verlag Opladen.
[5] H. Malissa, *Z. analyt. Chem.*, 1961, **181**, 39.

Zusammenfassung—Es wird eine neue Anwendung der relativkonduktometrischen Methode zur Kohlenstof- und Schwefel-Bestimmung aufgezeigt, die darauf beruht, durch langsame gelenkte Verbrennung eine differenzierte Erfassung einzelner Fraktionen des Kohlenstof- und Schwefelgehaltes organischer Substanzen zu ermöglichen.

Summary—A new application of the relative-conductimetric method for the determination of carbon and sulphur is described. The method consists in a slow programmed combustion and trapping of the different fraction. Thus it is possible to analyse the various fractions of the organic material for their carbon and sulphur content.

Résumé—Une nouvelle application de la conductimétrie relative au dosage du carbone et du souffre est décrite. La méthode consiste en une combustion lente er programmée à la suite de laquelle les différentes fractions sont recueillie. Il est ainsi possible de doser les diverses fractions de carbone et de soufre des substances organiques.

Copper^{II} catalysis of 8-acetoxyquinoline hydrolysis

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A METHOD for the precipitation of metal 8-hydroxyquinolates in homogeneous solution utilising the hydrolysis reaction of 8-acetoxyquinoline has recently been established.[1,2] The possibility that complexes of this reagent with metal ions might participate in such hydrolysis was considered in the present study of the effects of copper^{II} ion on the kinetics of the hydrolysis of 8-acetoxyquinoline.

EXPERIMENTAL

The 8-acetoxyquinoline, PFHS grade, was obtained from the Burdick and Jackson Laboratories and used without further purification.

Each of the hydrolysis reactions was carried out in a 20:1 mixture by volume of an appropriate aqueous buffer solution and a freshly prepared solution of 8-acetoxyquinoline in absolute ethanol. The ionic strengths of the stock aqueous buffers, with the exception of the most concentrated perchloric acid solution, were set at 0·10 by the addition of sodium perchlorate. An acetate buffer, a phosphate buffer, and two borate buffers having identical concentrations of borate ion, comprised the stock solutions of pH greater than 4. The other aqueous stock solutions were prepared from perchloric acid. Copper perchlorate was used in the preparation of the stock solutions containing copper ion.

Rate constants were measured spectrophotometrically. At appropriate time intervals, optical density measurements were taken of samples of the reaction mixtures, which were kept in a constant temperature bath maintained at 25·0°. Samples of the pH 3·05 reaction mixtures, initially 0·00002*M* in ester concentration, were transferred to a 10-cm absorption cell for measurement. Initial ester concentrations in the other reaction mixtures were in the range of 0·0001*M* to 0·0003*M*. Samples of these solutions were taken in a 1-cm absorption cell.

The conjugate acid of 8-acetoxyquinoline has an absorption maximum at 313·5 mμ ($\log \epsilon = 3{\cdot}77$). The free base has maxima at 313·5 mμ ($\log \epsilon = 3{\cdot}46$), 300 m$\mu$ ($\log \epsilon = 3{\cdot}56$), and 288 m$\mu$ ($\log \epsilon = 3{\cdot}62$). The variation of absorbancy at each of these wavelengths was in conformity with Beer's law in the concentration range studied. Hydrolysis to 8-hydroxyquinoline in solutions of pH less than 4 was followed at 313·5 mμ. Other rate measurements were made at 285·0 mμ.

A pK_a value of 3·14 ($\pm$0·05) for the 8-acetoxyquinolinium ion was determined by measuring changes in molar extinction coefficient with pH at 313·5 mμ.

KINETIC DATA FOR THE HYDROLYSIS OF 8-ACETOXYQUINOLINE

pH*	Measured first order rate constants, $min^{-1} \times 10^3$			Calculated† first order rate constants, $min^{-1} \times 10^3$		
	Cu^{2+} absent	0·0146*M* Cu^{2+}	0·0292*M* Cu^{2+}	Cu^{2+} absent	0·0146 *M*Cu^{2+}	0·0292*M* Cu^{2+}
	1·36‡					
1·05	0·36			0·37		
1·45	0·32			0·31		
2·05	0·41		0·46	0·40		0·44
2·35	0·57		0·70	0·56		0·69
2·67	0·82	1·04	1·30	0·84	1·08	1·32
3·05	1·34		3·4	1·33		3·4
4·72	2·64			2·66		
6·79	2·76			2·73		
8·80	3·5			3·5		
9·20	4·5			4·6		

* The pH reading at reaction completion for the copper-free reaction mixtures. The corresponding readings for the mixtures containing copper were 0·00–0·04 pH units lower, presumably because of copper chelation with 8-hydroxyquinoline. The largest pH differences were found at pH 2·67, where the ratios of initial ester concentration to hydrogen ion concentration were the highest. Kinetic calculations for any copper catalysed reaction accompanied by a substantial pH change were based only on the rate data collected during the first half of the reaction.

† See DISCUSSION

‡ In 0·9*M* perchloric acid.

The pH measurements were taken with a Beckman Model G pH meter standardised with Beckman pH 4 buffer solution for measurements above pH 4. A reaction solution of known acid concentration served to standardise the pH meter for measurements below pH 4. A Cary Model 11 spectrophotometer was used for the rate measurements.

DISCUSSION

The kinetic measurements established that the hydrolysis of 8-acetoxyquinoline is first order in 8-acetoxyquinoline. It was found that the variation of the first order rate constant with pH and copper concentration under the conditions studied could be expressed by a sum of terms corresponding to several catalysed and uncatalysed hydrolysis reactions. These included the hydrogen ion catalysed reactions of the ester and of the ester cation, the hydroxide ion catalysed hydrolysis of the ester, the hydrolysis without hydrogen ion or hydroxide ion catalysis but possibly involving intramolecular base catalysis by the amine function, and the hydroxide ion catalysed reaction of the 1:1 copper-ester complex. If K_a, the acid dissociation constant for the 8-acetoxyquinolinium ion, is introduced, the reaction terms may be written in the form

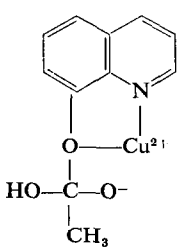
$$k = \frac{1}{(H^+) + K_a}\left\{k_1(H^+)^2 + K_a\left[k_2(H^+) + k_3 + \frac{k_4(OH^-)}{K_w} + \frac{k_5(OH^-)(Cu^{++})}{K_w}\right]\right\}$$

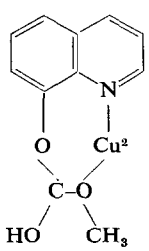
where

$k_1 = 0{\cdot}0017$ litre mol^{-1}min^{-1}
$k_2 = 0{\cdot}276$ litre mol^{-1}min^{-1}
$k_3 = 0{\cdot}00272$ min^{-1}
$k_4 = 1{\cdot}2 \times 10^{-12}$ mol litre^{-1}min^{-1}
$k_5 = 0{\cdot}00014$ min^{-1}

Values of the first order rate constant, k, calculated from the pH, the measured pK_a value of 3·14, and the k_1, k_2, k_3, k_4, and k_5 values given above, are listed in the table of kinetic data and compared with the measured constants.

The copper catalysed hydrolysis was found to be first order in 8-acetoxyquinoline (as the free base), first order in copper ion, and first order in hydroxide ion. It was surprising to find the order in hydroxide ion in view of the very low concentrations of this ion available for a reaction with the 1:1 copper-ester complex in the pH range studied. The order in hydroxide ion suggests that such a reaction would be a rate determining step if a mechanism analogous to one described[3] for the hydroxide ion catalysed hydrolysis reactions of other esters were followed. Possible structures for the reaction intermediate if some stabilisation by chelation is assumed are:





An investigation of the effects of other metal ions on the hydrolysis of 8-acetoxyquinoline is in progress.

Acknowledgement—Support of this research by the United States Public Health Service is gratefully acknowledged. The authors wish to thank Mr. Robert Brook for technical assistance.

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C. R. WASMUTH
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Summary—The hydrolysis of 8-acetoxyquinoline in dilute acid solution has been found to be subject to copper^{II} catalysis. The catalysed reaction is first order in 8-acetoxyquinoline (as the free base), first order in copper ion, and first order in hydroxide ion. It is proposed that a copper chelate is a reaction intermediate in the hydrolysis.

Zusammenfassung—Es wurde gefunden, dass die Hydrolyse von 8-Acetoxychinolin in verdünnter Säure durch Kupfer(II) katalysiert wird. Die katalytische Reaktion ist erster Ordnung in Bezug auf Acetoxin (als freie Base), Kupfer und auch Hydroxylion. Es wird angenommen, dass sich ein Kupferchelat als Zwischenprodukt bildet.

Résumé—L'hydrolyse de la 8-acétoxyquinoléine en solution acide dilué est catalysée par le cuivre(II). La réaction catalysée est du premier ordre à l'égard de la 8-acétoxyquinoléine (en tant que base libre), des ions cuivriques et des ions oxydriles. La formation d'un complexe du cuivre est proposée comme réaction intermédiaire lors de l'hydrolyse.

REFERENCES

[1] J. T. Corkins, R. F. Pietrzak, and L. Gordon, *Talanta*, 1962, **9**, 49; see also the preceding papers of this series.
[2] L. C. Howick and W. W. Trigg, *Analyt. Chem.*, 1961, **33**, 302.
[3] M. L. Bender, R. D. Ginger, and J. P. Unik, *J. Amer. Chem. Soc.*, 1958, **80**, 1044.

Talanta, 1962, Vol. 9, pp. 1063 to 1066. Pergamon Press Ltd. Printed in Northern Ireland

LETTERS TO THE EDITOR

Talanta

SIR,

Anybody with even a modicum of interest in analytical chemistry must, I think, peruse *Talanta* quite often. I wonder how many readers have been puzzled—as the writer is—by the meaning of this title. It certainly is more lively and appealing than the variety of *Archives—Memoirs—Acta—Journal—Zeitschrift* to which one has become accustomed since time immemorial—but what *does* it mean? Its editors and authors may be talented—the Journal may be worth a talent of gold—but why the plural Ταλαντα? And why was this title chosen? The writer dug out his old Greek dictionary, consulted the British Encyclopedia and the Oxford Dictionary, but no explanation was forthcoming. It might therefore perhaps not be out of place if the editor would give an explanation, either as a sub-title, or somewhere on the cover or in the table of contents, either of each issue or at least from time to time, and so end this tantalising frustration. At the birth of the Journal, an explanation was probably given to midwives and bystanders but many readers may have missed this stage and so perhaps *repetitio est mater studiorum.*

In spite, however, of this ethmological uncertainty, *vivat, crescat, floreat* Ταλαντα!

I am, Sir, Yours, *etc.*

WILLIAM STROSS

1, *Haydon Hill House,*
Bicester Road,
Aylesbury, Bucks. England.
16 *June* 1962.

Dear Dr. Stross,

Your enquiry, coupled with various other friendly enquiries in the past, leads me to believe that an explanation of the name of our Journal might be of interest to a wider public.

When we first projected the journal it was thought of as a sister journal to the already established *Tetrahedron.* It was, therefore, felt that it would be very appropriate if we had a Greek name to go with *Tetrahedron,* and one which was as closely associated with analytical chemistry as *Tetrahedron* is with organic chemistry. Apart from this, we felt that it would be a very considerable advantage to have a name which did not actually contain the terms "analysis" or "analytical"; for the purpose of indicating references, it was desirable to choose a title which could not be confused with any of the existing journals in analytical chemistry.

We consulted our Greek experts (we ourselves lay little claim to classical scholarship) and pointed out that the determination of the parts of a whole is fundamental to analytical chemistry. Their first suggestion was *Stoicheion.* We were tempted to accept this because it means quite precisely "element"; but we found that none of us could consistently spell the word correctly! The experts next said that the Greek word for a balance was *Talanta* (related to the Greek "talent" which, of course, was originally a weight of gold or silver). The rather obvious confusion with the word "talent", as used in its more conventional sense, appealed to our sense of humour, or whatever one might call it! We tried the name out on various people and they were rather intrigued by it; it seemed to fit in very well with *Tetrahedron*; and, therefore, we adopted it. I think it is true that most people do not understand the implication of it. But the cover design was, in its first rough draft, designed by us to include the Greek form of the name in order to give some sort of clue about the origin of the word.

Incidentally, the little vignette of balance which appears inside the cover is the result of a considerable amount of searching on the part of our Greek experts for an actual picture of a *Greek* balance. It is surprising how hard it was to track down one—we could get Egyptian balances and Roman balances, but this must be one of the very few authentic instances of an illustration of a Greek balance.

Tailpiece: It is curious to find how many people cannot spell the present name of the Journal correctly. We are quite startled to find how often people refer to it as "*Tantala*" and often speculate about what *would* have happened had we settled for *Stoicheion*!

Yours sincerely,

CECIL L. WILSON
(Editor-in-Chief)

The iodometric estimation of tin

SIR,

The accurate estimation of tin by titration with a standard solution of iodine has been attempted by many workers and the subject has, accordingly, a very large literature. No attempt is made here to survey the literature, although much of it has been consulted.

The method that seemed to us to be the most promising is that adopted in British Standard Method 1121, Parts 20 and 22; here the tin is reduced by aluminium foil in the presence of antimony, and the stannous tin is titrated with potassium iodate in the presence of potassium iodide. The method was applied in the following way: To a 250-ml conical flask, fitted with a side tube reaching to the bottom of the flask through which nitrogen (oxygen free) was passed throughout the experiment, was added an aliquot of stannic chloride solution containing 83·91 mg of tin, 40 ml of hydrochloric acid (sp. gr. 1·16), 2 ml of antimony chloride solution,* and sufficient water to bring the total volume to about 100 ml. One gram of aluminium foil was added in small amounts, the solution being kept warm to assist the reaction. After the last piece of aluminium had been added, the flask was attached to a reflux condenser and, when the aluminium had dissolved, the liquid was boiled for 30 min to redissolve the tin. The flask was then cooled, the condenser was removed, 10 ml of 10% potassium iodide were added, and the solution was titrated with standard 0·05*N* potassium iodate solution using starch as indicator. The results were reasonably consistent (28·68 $\pm$ 0·05 ml) but were 1% less than theoretical.

Similar results were obtained using nickel foil instead of aluminium and antimony. In these experiments strips of nickel foil (with a surface area of 12 in.^{2} and etched with a solution of hydrochloric acid and sodium chloride) were added and the solution was boiled under reflux for 2 hours before cooling and titrating.

Finally, Kolthoff's[1] method of reducing the tin with iron (reduced) and antimony was tried. This method gave consistent results and the titres were theoretical (*viz.* 1 ml of 0·05*N* iodate = 2·97 mg of tin). The experiment was carried out in a similar manner, and in the same apparatus, using 1 g of iron (reduced), added all at once, and 1 ml of antimony chloride solution, the solution being boiled under reflux until the iron had dissolved and for 20 min afterwards.

Järvinen[2] drew attention to the necessity of adding a sufficient excess of iron and we have found that with 180 mg of tin the titres are low, but that the theoretical result is obtained when the quantity of iron is doubled. If antimony is not present we found, as did Järvinen, that much larger amounts of iron are necessary. On the other hand, if the amount of hydrochloric acid is reduced from 40 ml to 10 ml, the theoretical titre is obtained using 1 g of iron. There was no blank in any of the above titrations.

* Add 5 ml of sulphuric acid (sp. gr. 1·84) to 500 mg of powdered antimony and fume the mixture until no free antimony remains. After cooling, dissolve the white residue in a mixture of 20 ml of hydrochloric acid (sp. gr. 1·16) and 50 ml of water, and dilute the solution to 100 ml.

Department of Mineralogy
British Museum (Natural History)
South Kensington
London S.W.7.
24 *July* 1962.

D. I. BOTHWELL
A. A. MOSS

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Sodium thiosulphate solutions

SIR,

IN a recent standard textbook,[1] the following statement appears, concerning the preparation of sodium thiosulphate solutions.

"Solutions of sodium thiosulphate keep very well indeed if made up in carbon dioxide-free boiled demineralized or distilled water. On no account should carbonates be added to the solution to make it keep better as recommended by some authors. The addition of carbonates actually has the reverse effect."

We have habitually made an addition of 0·01 % w/v of sodium carbonate in preparing thiosulphate solutions, and it has not been our experience that this is deleterious. For example, a solution prepared in distilled water[2] in equilibrium with atmospheric carbon dioxide and containing 0·01 % sodium carbonate, which was carefully standardised potentiometrically against potassium iodate and cross checked with potassium bromate, had a factor of 1·0077 ± 0·0002 on 6th June 1955. The solution was stored in a polythene-screw-capped brown glass Winchester. Rather more than seven years later this solution was independently restandardised, and had a factor of 1·0068 ± 0·0002 on 1st August 1962. The solution remained perfectly clear and free from sediment.

E. BISHOP
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Exeter
Devon, England
11 *August* 1962

REFERENCES

[1] C. L. Wilson and D. W. Wilson (Editors), *Comprehensive Analytical Chemistry*, Volume 1B, Elsevier Publishing Co., Amsterdam, 1960. p. 253.
[2] E. Bishop and J. R. B. Sutton, *Analyt. Chim. Acta*, 1960, **22**, 590.

The oxygen flask method at low halogen levels

Sir,

THE use of the Oxygen Flask method for the determination of halogens in organic substances has been encouraged in numerous publications[1] since its re-introduction in 1955. It is noteworthy however, that no systematic study of the limitations of the method has been made. The writer wishes to stimulate critical consideration of the combustion conditions and the blank values in this method, especially with regard to its possible application at halogen levels below 10^{-5} g equiv.

The very nature of the combustion conditions engenders doubt about their efficiency; and experience of the method in routine use indicates that liquid, refractory, and high-halogen-content substances are not always completely combusted. Various expedients facilitate their correct analysis, but these detract from the value of the determination as a routine method. In particular, liquid substances have no universally satisfactory way of combustion, the probability of the escape of vapour before or during burning being high in all the published methods.

The blank value from the substance wrapping material has hitherto either been ignored or been assumed to be small and constant. It is certain, however, that this value is not very reproducible, and is often a serious limiting factor of the accuracy of the method. This is particularly so at the halogen level mentioned above, where the blank value amounts at a minimum to approximately 5 % of this level (see Table).

The magnitude and variability of the value are increased if finger stalls are not worn by the analyst. If a halogen-differentiating finish is coupled with the method,[2] the blank value makes bromide and iodide analysis possible but chloride analysis impossible. The reagents used in the method contribute a constant blank of the order of 8×10^{-8} g equiv of Cl^-, which is of little significance The avoidance of a wrapping material, as in carbon determinations,[1] is not recommended on account of the poor combustion conditions, and reduction in the material size introduces serious handling problems.

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Material	Average Cl^- content, *g equiv* $\times 10^{-7}$
(*a*) "Whatman" filter paper, No. 541 (1·5 in².)	7
(*b*) Double water washed (*a*) (1·5 in².)	5
(*c*) "Whatman" filter paper, No. 1 (1·5 in².)	5
(*d*) "Kleenex" tissue (1·5 in².)	14
(*e*) Tracing paper (1·5 in².)	18
(*f*) "Sellotape" (1·0 in².) + fuse of (*a*) (0·5 in².)	4 + 2
(*g*) "Eli Lilly" Gelatin Capsule No. 5 + (*a*) (1·5 in².)	8 + 7
(*h*) "Parke, Davis" Gelatin Capsule No. 5 + (*a*) (1·5 in².)	3 + 7

In conclusion, it is recommended that a tube combustion procedure be generally adopted at this halogen level. It provides more ideal combustion conditions, a constant reagent blank value, and relatively easy handling of liquid substances, in comparison with the Oxygen Flask method. Even at the micro-determination halogen level (5×10^{-5} g equiv), a tube combustion procedure is recommended.

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28 *September* 1962

REFERENCES

[1] A. M. G. Macdonald, *Analyst*, 1961, **86**, 3.
[2] D. G. Newman and C. Tomlinson, *Mikrochim. Acta*, 1961, 73.

Talanta, 1962, Vol. 9, pp. 1067 to 1070. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEWS

Monographs on the Radiochemistry of Elements. The Sub-Committee on Radiochemistry, National Academy of Sciences. National Research Council, U.S.A.

THIS is a series of monographs on the radiochemistry of the elements. Each monograph is written by an authority on the radiochemistry of the particular element, and has been written to a standard format. Contents include general reviews of the inorganic, analytical and radiochemistry of the element, a table of its isotopes, a review of properties of particular interest to radiochemists, counting techniques pertinent to the element under consideration, and a collection of detailed radiochemical procedures.

The major part of the monograph is taken up by the latter section, and a critical selection of the known radiochemical techniques for each element has obviously been made. A number of the procedures have originated in Atomic Energy Establishments and it is possible that their appearance in these monographs marks their first open publication. The literature has, in some of the monographs, been covered up to 1962.

This series will be of particular interest to the radiochemist or the analytical chemist. It will also be of value to the biochemist and the physicist who often use radiochemical techniques in the solution of specific problems.

The most recent additions to the series now available are:

The Radiochemistry of Silicon. W. T. MULLINS and G. W. LEDDICOTTE. January, 1962. $0.50.
The Radiochemistry of Osmium. G. W. LEDDICOTTE. October, 1961. $0.50.
The Radiochemistry of Iridium. G. W. LEDDICOTTE. October, 1961. $0.50.
The Radiochemistry of Platinum. G. W. LEDDICOTTE. October, 1961. $0.50.
The Radiochemistry of Tellurium. G. W. LEDDICOTTE. October, 1961. $0.50.
The Radiochemistry of Tungsten. W. T. MULLINS and G. W. LEDDICOTTE. September, 1961. $0.50.
The Radiochemistry of Vanadium. J. L. BROWNLEE, JR. December, 1960. $0.75.
The Radiochemistry of Gold. J. F. EMERY and G. W. LEDDICOTTE. May, 1961. $0.50.
The Radiochemistry of Germanium. J. A. MARINSKY. July, 1961. $0.50.
The Radiochemistry of Lead. W. M. GIBSON. August, 1961. $1.75.
The Radiochemistry of Niobium and Tantalum. E. P. STEINBERG. August, 1961. $0.75.
The Radiochemistry of Selenium. G. W. LEDDICOTTE. April, 1961. $0.50.
The Radiochemistry of Polonium. P. E. FIGGINS. January, 1961. $0.75.
The Radiochemistry of the Transcurium Elements. G. H. HIGGINS. October, 1960. $0.50.
The Radiochemistry of Cobalt. L. C. BATE and G. W. LEDDICOTTE. September, 1961. $1.00.
The Radiochemistry of Potassium. W. T. MULLINS and G. W. LEDDICOTTE. November, 1961. $0.50.
The Radiochemistry of Silver. D. N. SUNDERMAN and C. W. TOWNLEY. November, 1961. $0.75.
The Radiochemistry of Aluminium and Gallium. J. E. LEWIS. April, 1961. $0.50.
The Radiochemistry of Titanium. CHONG KUK KIM. March, 1961. $0.50.

In the same series the following publications dealing with radiochemical techniques have appeared:

Low-level Radiochemical Separations. T. T. SUGIHARA. April, 1961, $0.50.
Separations by Solvent Extraction with Tri-n-octylphosphine Oxide. J. C. WHITE and W. J. ROSS. February, 1961. $0.75.
Liquid-Liquid Extraction with High Molecular Weight Amines. F. L. MOORE. December, 1960. $1.00.
Rapid Radiochemical Separations. Y. KUSAKA and W. WAYNE MEINKE. December, 1961. $1.25.

The following publications are now also available:

Radio-active Contamination of Materials Used in Scientific Research. J. R. DEVOE. Publication 895. 1961.
A Cross-Referenced Index of Radiochemical Teaching Experiments Applicable to Chemistry. G. R. CHOPPIN. Publication 905. 1961.

R. J. MAGEE

Progress in Nuclear Energy, Series IX: Analytical Chemistry, Volume 2. Edited by C. E. CROUTHAMEL. Pergamon Press Limited, Oxford, 1961. pp viii + 400. £5. 0. 0.

IT will be recalled that Volume 1 of Progress in Nuclear Energy, Series IX, reproduced the analytical chemistry papers presented at the 1958 Geneva Conference on *Peaceful Uses of Atomic Energy*. Volume 2 comprises eight review articles covering a wide range of subject matter, as follows:

1. *Recent Advances in Counting Techniques*, by C. Gastrousis, R. Heinrich and C. E. Crouthamel (79 pages)
2. *Magnetic Resonance Spectroscopy, Applications of Electron Spin Resonance Spectroscopy to Organic and Inorganic Chemistry*, H. A. Elion and L. Shapiro (75 pages).
3. *Recent Advances in the Separation and Analysis of the Transuranium Elements*, by D. C. Hoffman (43 pages).
4. *Applications of Liquid-Liquid Extraction in Inorganic Chemistry*, by D. F. Peppard (23 pages).
5. *Flame Photometry and Atomic Absorption Spectroscopy*, by J. W. Robinson, (32 pages).
6. *Recent Advances in Ultraviolet, Visible and Infrared Spectrometry*, by J. C. White, (55 pages)
7. *Particle Interactions with Matter; Backscattering and Excitation of Characteristic X-rays*, by R. H. Müller (24 pages).
8. *Ion Exchange Chromatography*, by J. E. Salmon (42 pages).

As these titles suggest, the phrase "nuclear energy" has been interpreted in its widest sense; indeed, Chapters 2, 5 and 8 touch only incidentally on the nuclear energy field, though it can be argued with considerable truth that virtually every element has occupied the interest of nuclear scientists in one way or another and therefore commanded the attention of their analytical colleagues. The present volume should be of wide appeal and several of the chapters will be of value to analytical chemists outside the nuclear field.

Chapter 1 deals with the gas ionisation proportional spectrometer, solid state spectrometry and scintillation spectrometry. It strikes an excellent balance between theory and practice and will be welcomed by the chemists in the radiochemical field who constantly struggle to keep abreast of the advances achieved by their colleagues in counting techniques. Chapter 2 is an eminently readable introduction to magnetic resonance and electron spin resonance spectroscopy and indicates clearly the potential of a technique which as yet remains a highly specialised "tool of the future" to the vast majority of analysts. The separation and determination of the transuranium elements have presented some formidable problems and in Chapter 3 Hoffman reviews a now extensive literature in a balanced and workmanlike manner.

Peppard's chapter on liquid-liquid extraction, though rather surprisingly the shortest of the volume, is a scholarly and concise presentation. Dealing almost entirely with nuclear chemistry, its principal objective is to familiarise the analyst with the wealth of solvent extraction data which has become available in recent years and to discuss critically its potential analytical value. Inevitably the principal coverage is accorded to the wide variety of acidic phosphorus esters and organic phosphinic acids which have received such extensive study. The mode of operation and practical application of these substances is presented with commendable clarity.

In Chapter 5, Robinson reviews in detail the present status of flame photometry (with particular reference to high temperature flames) and atomic absorption spectroscopy. The latter is discussed under the heading *Recent Advances in Flame Photometry* and could give rise to the misleading impression that atomic absorption spectrometry is limited to flame excitation. Chapter 6, by White, reviews recent advances in ultraviolet, visible and infrared spectrometry under three main headings: *Status of Ultraviolet and Visible Spectrophotometric Methods for Selected Elements, Advance in Infrared Absorption Analysis* and *Absorption Spectrophotometry of Molten Salts*. The first two call for little comment but the third is a most valuable contribution. It considers in detail the many practical problems of obtaining spectra of melts. It is supported by some excellent diagrams and should be compulsory reading for those wishing to enter this relatively new field.

In Chapter 7, *β-particle Interactions with Matter*, the reader is led easily through the many facets of β-backscattering and the β-particle excitation of *bremsstrahlung* and characteristic X-rays. The analytical applications of the latter *vis-a-vis* the conventional X-ray methods are critically considered. The chapter is mainly of a broad general nature and could well have some appeal at student level.

Ion Exchange Chromatography, the subject of Chapter 8, has been a particular favourite of authors of review articles during the past decade and apart from some recent applications in the period 1957–1960 the present contribution contains little that cannot be readily found elewhere. The author has recognised this limitation and has incorporated a *résumé* of the basic operational principles of the diverse forms of ion exchange and the whole is presented clearly and succinctly.

Undoubtedly specialist readers in the various fields reviewed in this volume will find grounds for justifiable criticism on matters of detail, but on the whole the book is intended to command the attention of a much wider audience interested in, but not necessarily closely associated with, those aspects of analytical chemistry which have received such impetus from the demands of nuclear science. To such an audience the book can be recommended; it is well produced and contains copious reference to the original literature. A notable omission from the work is electrochemical analysis, and it is to be hoped that this will be rectified in a subsequent volume.

J. K. FOREMAN

Microdiffusion Analysis and Volumetric Error. E. J. CONWAY. 5th revised edition, Crosby Lockwood and Son Ltd., London, 1962. Pp xviii + 467, 42s.

IN a review of the 4th revised edition of *Microdiffusion Analysis* (*Talanta*, 1959, **2**, 98), the present reviewer drew attention to the responsibility of an author to his readers to provide a periodically revised text. The continued success of a book depends very much on how effective the revision is. With Professor Conway's book, the publishing history reflects how well the techniques of microdiffusion analysis have been received by successive generations of chemists and biochemists, and how great is the present interest in the subject.

A comprehensive review of this book is uncalled for. The reviewer has no intention of preaching to the converted, but for those who have little or no experience of microdiffusion analysis, it may suffice to state that here is the one authoritative text on the subject which not only contains all the important and relevant material from the earlier editions, but also has the advantage of containing much new material incorporated into the text since the 4th edition appeared in 1957. The revision is by no means superficial; Professor Conway lists in his preface the several new applications of the technique which are now included in the text. Attention has also been given to developments in the design and construction of the microdiffusion cells. This revision will be welcomed by all those familiar with the methods of microdiffusion analysis not only because of the increased utility of the book to themselves, but also because they can confidently recommend an up-to-date account of the technique to their students and colleagues as yet uninitiated to the methods.

W. I. STEPHEN

The Collected Works of Irving Langmuir; Vol. 7, Protein Structures; Vol. 8, Properties of Matter; Vol. 9, Surface Phenomena. General Editor, GUY SUITS. Pergamon Press Limited, Oxford, 1961. Pp xlii + 227; xxix + 251; and xxi + 521. 100/- net per volume.

THE publication of the works of Irving Langmuir in twelve volumes is a worthwhile task only because of the importance of Langmuir's contributions to the subjects which he investigated. The importance of his work stems not only from the clarity and brillance of his publications but also from the inspiration and influence which they had on others who followed after him. Perhaps the most valuable effect of the present volumes will be to induce more people to read some of Langmuir's work in the original form rather than to rely on the accounts condensed and distilled from one textbook to the next—a process which may retain the essence but certainly destroys the flavour of his work.

Each volume has one or two introductory chapters by authorities in the respective fields. Dr. Harry Sobotka in Volume 7 gives a fairly extensive survey describing the influence of Langmuir's work on protein structures on subsequent research. Dean Henry Eyring's introduction to Volume 8 is more personal in character and Volume 9, which is divided into two parts, has articles by Professor N. K. Adam relating to evaporation, condensation and adsorption and by Dr. W. A. Zisman on monomolecular films.

The volumes are clear, readable and well-produced. The division of the papers into the respective volumes is perhaps not ideal; *e.g.*, some of those in Volume 8 are very closely related to many in Volume 9, but the problem of the appropriate grouping of the work is obviously difficult. The method of charging the same sum for each volume seems completely unjustifiable except on grounds of administrative convenience. The price of 100/- for a substantial volume like No. 9 seems high enough but, since Volumes 7 and 8 are considerably smaller, one is left with the conclusion that they are grossly over-priced.

C. KEMBALL

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C. KEMBALL

The Determination of Stability Constants. FRANCIS J. C. ROSSOTTI and HAZEL ROSSOTTI. McGraw-Hill Book Co. Inc., New York, 1961. pp. 425. 97s.

MANY of the remarkable advances in theoretical inorganic chemistry in the last decade rest heavily on the results of a great deal of experimental work on the determination of the stability constants of metal complexes in solution. This book gives an account of the many experimental methods which may be used and describes in detail the computational procedures whereby stability constants are derived from the primary experimental results. It is the first authoritative work on this subject. The authors are specialists who have been closely associated with two of the major schools of solution co-ordination chemistry.

There are eighteen chapters. The first five, which include a brief survey of background and basic principles, are mainly concerned with the generalised methods of evaluation of step formation constants in simultaneous equilibria. The use of secondary concentration variables, "degree of formation" and "ligand number", and of graphical methods such as that of "normalised curve fitting" are treated in detail. Chapters 6-15 deal with the various physico-chemical techniques which may be applied to stability constant determination in mononuclear systems. All make use of some measurable property of the system which changes in a definite way with the degree of complex formation. Those described include potentiometry, solubility, liquid-liquid partition, ion-change and optical and kinetic methods. The final three chapters are concerned with mixed and polynuclear systems.

Throughout, the treatment is critical. For example, some indication of the suitability of a particular experimental or computational method in different circumstances is usually given. It is the authors' view that in the past much work has been poorly designed and that mathematical analysis of data, often incomplete, has not always been carefully carried out. Most of the common pitfalls can be avoided by a careful reading of this volume. For example, the importance of covering a wide range for each of the concentration variables, where several simultaneous equilibria are involved, is stressed, as is also the need for maintaining an environment of constant ionic strength for the control of activity coefficients. The choice of background electrolyte for a given investigation, and the significance of stoicheiometric, as compared with thermodynamic, equilibrium constants are discussed.

While the stimulus for this book has unquestionably been the rapid and growing interest in the solution chemistry of metal complexes, the mathematical techniques described are, of course, applicable to any system of equilibrium, *e.g.*, dissociation of acids and bases, ion association, hydrogen bond formation and equilibria involving relatively large aggregates of molecules and ions such as micelles, *etc.*, though not all of these are treated specifically. Rather more might have been included on measurements in mixed and non-aqueous solvents.

For the sake of exactness the authors have adopted a rather formal mathematical presentation requiring the use of a great number of different symbols, many of them confusingly alike. Probably this was unavoidable; it does not, however, make for easy reading, and most readers would welcome a greater use of illustrative examples.

The bibliography seems very comprehensive and the book is attractively produced. It is intended for research workers, in a variety of fields, actively concerned with equilibria in solution; few can afford to be without it.

S. M. NELSON

Talanta, 1962, Vol. 9, pp. 1071 to 1074. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

(Material for this Section should be sent directly to the Associate Editor)

AUSTRALIA

Tuesday–Friday 20–23 *August* 1963: **Fourth Australian Spectroscopy Conference:** *Spectroscopy Committee of Australian Academy of Science.* Australian National University, Canberra.

The Conference will cover all aspects of pure and applied spectroscopy. It is hoped to have separate sessions on the following fields of spectroscopy: Atomic Emission, Atomic Absorption, Infrared and Raman, Microwave, Nuclear Magnetic, Nuclear Quadrupole and Electron Spin Resonance, Molecular Electronic, Spectra of Molecules of Biological Interest, Astrophysical Spectroscopy and Mass Spectrometry. The use of spectroscopy as an analytical tool will be featured.

Conference papers should represent original and unpublished work. It is hoped to allow 20 min for presentation of papers and 10 min for discussion. Titles of proposed papers should be submitted before 28 February 1963 and abstracts (150 to 200 words) before 15 May 1963 to the Secretaries for Collection and Publication of Abstracts, Dr. C. H. WILLIAMS and Mr. D. J. DAVID, Division of Plant Industry, C.S.I.R.O., Canberra. There will also be a limited number of invited review papers. The principal invited speaker will be Dr. G. HERZBERG, F.R.S., Director, Division of Pure Physics. National Research Council of Canada.

AUSTRIA

Friday 14 *December* 1962: **Review of Catalysts in Determination of Carbon and Hydrogen in Organic Compounds:** Dr. G. KAINZ: *Österreichische Gesellschaft für Mikrochemie.* Wien.

The *Österreichische Gesellschaft für Mikrochemie* and *Verein Österreichischer Chemiker* announce that they will sponsor an **International Congress on Analytical Chemistry** during the first week of *October* 1965.

There will be 6 plenary lectures and 80 other lectures, the main topics being *Measurements in the Range* 10^{-6}–10^{-12} g and *Automation in Analytical Chemistry.* Application has been made for the patronage of I.U.P.A.C. for the Conference.

HUNGARY

Friday–Saturday 21–22 *December* 1962: **Analytical Chemistry Congress:** Budapest.

The following papers will be delivered after the opening of the Congress by Professor E. SCHULEK:

Recent Developments in Spectrum Analysis.	T. TÖRÖK
New Methods in Spectrum Analysis: Use of the Plate Electrode and A.C. Arc Examination.	T. KANTOR
Problems of Enrichment in Spectrum Analysis of Solutions.	O. SZAKÁCS
Recent Spectrophotometers.	G. SVEHLA
Use of Spectrophotometry in Steroid Hormone Research.	A. SZABÖ
Differential Spectrophotometry.	A. PÁLL and G. SVEHLA
Use of Atomic Absorption Spectrophotometry in Metal Analysis.	L. KOLTAI and G. SVEHLA
Spectrophotometric Method for Determination of Carbon Content of Organic Compounds	L. TÖRÖK
New Methods in Radiochemical Analysis.	E. KÖRÖS
Recent Developments in Thermogravimetric Analysis.	F. PAULIK
Special Instruments of Organic Analysis.	L. MÁZOR
Automatic Titrimeters	I. BUZÁS
Analytical Use of Catalytic Reactions.	J. LASZLOVSZKY
Recent Developments in Polarographic Analysis.	G. FARSANG
Recent Developments in Gas Chromatography.	J. TAKÁCS

Further details can be obtained from Dr. L. MÁZOR, Institute for General Chemistry, Technical University, Budapest XI, Gellért tér 4,

Die **V. Ungarische Tagung für Emissionsspektralanalyse** wurde von 9 bis 11 August 1962 in Miskolc abgehalten (Siehe *Talanta*, 1962, **9**, 402 und 628).

Zusammenfassende Vorträge:

Die Anhaltspunkte und Möglichkeiten der heimischen Einführung der direktanzeigenden optischen Emissionsspektralapparate.	T. TÖRÖK
Die Bedeutung der Emissionsspektroskopie im Eisenhüttenwesen.	L. PAKSY
Uber die wirtschaftliche Bedeutung der Spektralanalyse für die Stahlindustrie.	B. WESZPRÉMY
Die Spektralanalyse von Schlacken.	E. GEGUS
Spektralanalyse der Reinmetalle.	S. KEREKES
Die Rolle der spektroskopischen Materialprüfung in der Eisen- und Stahlindustrie.	G. SZIKORA

Die Texte dieser Hauptvorträge werden in der Ungarischen Zeitschrift fur Hüttenwesen (*Kohászati Lapok*) erscheinen.

Originale Kurzvorträge:

Erfahrungen und Anwendungsmöglichkeiten des ARL-Quantovacs.	T. VOGEL
Die Anwendung einer Schmelzelectrode zur spektral-analytischen Bestimmung kleiner Mengen von Antimon und Arsen in Blei.	B. HOLIŃSKA
Vakuumspektrometrische Qualitätskontrolle von Stahl.	H. EISCHER
Verstellbare Blende mit Stufenfilter zur qualitativen Spektralanalyse.	O. SZAKÁCS
Spektrographische Untersuchung archäologischer Funde aus der Kupfer- und Bronzezeit.	K. ZIMMER, Z. L. SZABÓ und P. PATAY
Die Spektralanalyse von Aluminiumlegierungen unter Anwendung von geeigneten Analysenverfahren.	Z. CZAJKA
Eine neue, Schwärzungsunterschieden der Manganlinien beruhende Methode zur Bestimmung des Mangangehaltes von Aluminiumlegierungen—I.	L. PÉTER
Höhere Nachweisempfindlichkeit von Eisen bei Untersuchungen mit der doppelt rotierenden Funkenstrecke in Argon.	W. GUTTMANN
Eine spektrographische Methode zur quantitativen Bestimmung von Kupfer, Zink und Blei in Erzen.	M. GRALIKOWSKI and J. PODSIADLO
Probenahme bei der Spektralanalyse.	M. GÁL
Eigenschaften und Verwendung der hochohmigen Spektralkohlenelektroden.	S. MELUŠ and S. ORSZÁGH
Anwendungen der Röntgenfluoreszenz-Spektrometrie in der Stahlindustrie.	H. EISCHER
Über eine erhebliche Verkürzung der Zeitdauer der spektrographischen Schnellanalysen.	W. KLIMECKI

Die Texte dieser Kurzreferate erscheinen in der Decembernummer der Ungarischen Zeitschrift for Chemie (*Magyar Kémiai Folyoirat*).

Weitere Auskunft ist in Dr. K. ZIMMER, G.T.E., V. Szabadság tér 17, Budapest, zu erhalten.

UNITED KINGDOM

Wednesday 19 *December* 1962: **Mass Spectrometry:** *Institute of Physics and Physical Society.* Imperial College of Science and Technology, London. 9.30 a.m.

The provisional programme is as follows:

New Instrumental Techniques of Isotope Analysis.	H. W. WILSON
Field Emission and Ionisation Studies.	A. J. B. ROBERTSON
Study of Ions and Radicals in Flames.	T. M. SUGDEN
Theory of Mass Spectra.	G. R. LESTER
Application of High Resolution Techniques in Mass Spectrometry.	R. D. CRAIG
Mass Spectrometric Analysis of Very Small Quantities of the Noble Gases.	M. H. DODSON

The Honorary Secretary for the Meeting is Mr. R. M. S. HALL, Central Electricity Generating Board, Research Laboratories, Cleeve Road, Leatherhead.

Thursday 10 *January* 1963: **Annual General Meeting:** *Western Section, Society for Analytical Chemistry*, followed by Joint Meeting with *Bristol and District Section, Royal Institute of Chemistry:* **New Developments in Chelatometry—A Review of Methods and Reagents related to EDTA:** T. S. WEST. University, Bristol. 5.30 p.m. and 6.30 p.m.

Wednesday 23 *January* 1963: **London Discussion Meeting:** *Microchemistry Group, Society for Analytical Chemistry. The Feathers*, Tudor Street, London, E.C.4. 6.30 p.m.

Thursday 24 *January* 1963: **Recent Advances in Polarography:** G. F. REYNOLDS: *Midlands Section, Society for Analytical Chemistry* and *Birmingham and Midlands Section, Royal Institute of Chemistry*. North Staffordshire Technical College, Stoke-on-Trent. 7.00 p.m.

Friday 25 *January* 1963: **Annual General Meeting:** *Scottish Section, Society for Analytical Chemistry*. Glasgow. 1.30 p.m.

Saturday 26 *January* 1963: **Annual General Meeting** followed by **Address of Retiring Chairman,** Mr. J. MARKLAND: *North of England Section, Society for Analytical Chemistry. Old Nags Head Hotel*, Lloyd Road, Manchester. 2.15 p.m.

Wednesday–Thursday 17–18 *April* 1963: **First International Meeting in Questioned Documents.** London School of Pharmacy.

The draft programme is:

1. *Writing Materials—Paper/Instruments/Inks.*
2. *Laboratory Examinations—Chemical/Photographic/Optical.*
3. *Recent Advances/Problems in Q.D. Examinations.*

The Role of the Q.D. Examiner as an Expert Witness.

Further information is available from P. G. BAXTER, 55 Cresent Road, Brentwood, Essex, England or from O. HILTON, 15 Park Row, New York 38, N.Y., U.S.A.

Wednesday–Tuesday 17–23 *July* 1963: **Fifth International Pesticides Congress.** Friends House, West Central London.

The programme will be divided into six Topics, one of which is entitled *Pesticide Residue Analysis.* The papers under this Topic will be concerned with modern analytical methods, special emphasis being given to those techniques having a wide application to current problems. The subjects envisaged are:

1. *Clean-up Processes* (including *Oxygen-Flask Combustion*).
2. *Biological and Enzymatic Methods.*
3. *Infrared Methods.*
4. *Chromatographic Methods.*
5. *Electroanalytical and New Methods.*

Opening papers for the above subjects are being arranged and other papers relating to new work in any of them are also invited. Details of (a) title of paper, (b) heading under which it is offered, and (c) three copies of a summary (150–250 words) must be sent, not later than 2 January 1963, to either Dr. H. EGAN, Laboratory of the Government Chemist, Clement's Inn Passage, London, W.C.2 or to Dr. E. A. PARKIN, Pest Infestation Laboratory, London Road, Slough, Bucks. Time allowed for presentation will be up to 20 min, and 5–10 min will be allowed for discussion.

General enquiries about the Congress should be directed to the Congress Honorary Secretary, Lt.-Col. F. J. GRIFFIN, 14 Belgrave Square, London, S.W.1.

British Standards Institution announces the following **Revised British Standard:**

B.S. 1427: 1962: *Routine control methods of testing water used in industry* (Price: 12s.6d.). This covers methods of test for the following:

1. Alkalinities
2. Aluminium
3. Ammonia (free and saline)
4. Calcium
5. Chloride
6. Residual chlorine (free and total)
7. Colour
8. Dissolved oxygen
9. Dissolved salts
10. Electrical conductivity
11. Free carbon dioxide
12. Hardness
13. Hydrazine
14. Iron
15. Magnesium
16. Nitrite
17. pH value
18. Phosphates
19. Silica
20. Specific gravity
21. Sulphate
22. Sulphite

UNITED STATES OF AMERICA

Tuesday 8 *January* 1963: **Analysis of Solids by Vacuum Spark Mass Spectroscopy:** A. J. AHEARN: *New York Section, Society for Applied Spectroscopy*. Hotel Manhatten, 44 Street and 8 Avenue, New York. 8.00 p.m.

Monday–Thursday 21–24 *January* 1963: **International Symposium on Advance in Gas Chromatography.** Sheraton-Lincoln Hotel, Houston, Texas.

The programme is as follows:

Monday morning 21 *January*	
A Sensitive Ionisation Cross-Section Detector for Gas Chromatography.	J. E. LOVELOCK
Use of Catalytic Combustion Filaments for Qualitative Gas Chromatography.	O. F. FOLMER
A New Radioactive Gas Chromatographic Detector for Identification of Strong Oxidants.	B. J. GUDZINOWICZ
Monday afternoon, 21 *January*	
Capillary Columns—Trials, Tribulations and Triumphs. Informal Conference	D. H. DESTY
Gas Chromatography and Inorganic Chemistry.	C. S. G. PHILLIPS
A New Column System for Gas Chromatography.	R. P. W. SCOTT
A New Concept in Gas Chromatography.	H. R. FELTON
Tuesday morning, 22 *January*	
Theoretical and Practical Considerations on Choice of Solvent and Filling of Analytical and Preparative Columns.	E. BAYER
Rapid Scanning Mass Spectrometry: Continuous Analysis of Fractions from Capillary Gas Chromatography.	J. A. DORSEY
Studies on Efficiency of Packed Gas Chromatographic Columns.	D. D. DEFORD
Recirculated Column for Preparative-Scale Gas Chromatography.	M. J. E. GOLAY
Tuesday afternoon, 22 *January*	
Diffusion and Mass Transfer Coefficients in Packed Gas Chromatographic Columns.	J. H. PURNELL
Advances in the Theory of Plate Height in Gas Chromatography.	J. C. GIDDINGS
Storage and Complete Automatic Computation of Gas Chromatographic Data.	H. W. JOHNSON, JR.
Wednesday morning, 23 *January*	
Spreading of "Air Peaks" in Capillary and Packed Gas Chromatographic Columns.	J. H. KNOX
Capillary Adsorption Columns.	R. D. SCHWARTZ
New Types of Columns in Gas Chromatography.	I. HASLASZ
Wednesday afternoon, 23 *January*	
A Simple Compact Gas-Radio Chromatogram.	A. T. JAMES
Radio Assay of Gas Chromatographic Compounds Labelled with Tritium.	A. KARMEN
Quantitative Aspects of Gas Chromatographic Separations in Biological Studies.	E. C. HORNING
Thursday morning, 24 *January*	
Analysis of Flavours by Gas Chromatographic Techniques.	A. I. M. KEULEMANS
Electron Capture Spectrometry of Biological Compounds.	S. R. LIPSKY
Determination of Lead Alkyls by Electron Capture.	H. J. DAWSON
Applications of the Methylene Insertion Reaction to Component Analysis of Hydrocarbons.	I. DVORETZKY

Further information may be obtained from Dr. A. ZLATKIS, Department of Chemistry, University of Houston, Texas.

Talanta, 1962, Vol. 9, p. 1075. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Contribution to the basic problems of complexometry—Part XI. Determination of titanium, iron and aluminium in the presence of each other: RUDOLF PŘIBIL and VLADIMÍR VESELÝ. (1 *October* 1962)

Improved method for calculation of error in quantitative spectrophotometric measurements: G. SVEHLA, A. PALL and L. ERDEY. (1 *October* 1962)

The oxygen flask method at low halogen levels: C. TOMLINSON. (1 *October* 1962)

Use of the argon gas chromatograph in the quantitative determination of carbon in steel: A. K. GALWEY. (1 *October* 1962)

Determination of methylol group in phenolic resins by titration with sodium methoxide and infrared absorption spectroscopy: NAOKI YOSHIMI, MASAYOSHI YAMAO, and SHIGEYUKI TANAKA. (4 *October* 1962)

New principle of activation analysis separations I. Theory of substoicheiometric separations: JAROMÍR RŮŽIČKA and JIŘÍ STARÝ. (9 *October* 1962)

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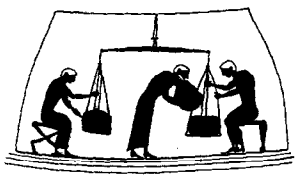
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ERRATA

Page 228, *authors of paper: for* Ruzikča *read* Růžička.
Page 492, *title of paper:* for 1-dithiocarboxy-3-methyl-5-phenyl-pyrazoline *read* 1-dithiocarboxy-3-methyl-5-phenyl-pyrazole.
Page 633, *line* 20: *for* $k = M\alpha^{-1}k_{MF}$ *read* $k = \eta\alpha^{-1}k_{j\ F}$.
Page 640, *reference* 120: J. Lustěnec, J. Krekule u. V. Pokorná, *Biol. Plant.* (*Praha*), 1960, **2**, 223.
Page 713, *caption to Fig.* 3: *for* Silver-Bromopyrogallol colour red system *read* Silver-Bromopyrogallol red colour system.
Page 824, *title of paper: for* Oxidation of cobalt^{III} with iron^{II} chloride in 2,2′-bipyridyl *read* Oxidation of cobalt^{II} with iron^{III} chloride in 2,2′-bipyridyl solutions.
Page 898, *line* 15: *for* The excitation process in the positive column the collisions of electrons with gas molecules *read* The excitation process in the positive column results from the collisions of gas molecules.

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Page 898, *line* 15: *for* The excitation process in the positive column the collisions of electrons with gas molecules *read* The excitation process in the positive column results from the collisions of gas molecules.

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ERRATA

Page 1, last line of Summary: the formula should read $(NH_4)_3[Sc(C_8H_6O_3)_3]$.

Page 9, footnote: the reference should read *Zhur. analit. Khim.*, 1959, **14** (5), 574.

Page 26, line 2: for *Sajó method*[4] read *Sajó method*[5].

Page 76, footnote: the reference should read *Talanta*, 1961, **8**, 720.

Page 85: reference 1 should read G. Frederick Smith, *Talanta*, 1962, **9**, 65.

Page 176: the legend for Fig. 1 is under Fig. 2 and *vice versa*.

Page 282: lines 25–27 should be deleted.

Page 225: the author in reference 4 should read J. S. HETMAN.

Page 328: the legend for Table II should read *Determination of copper in presence of nickel*^{II} *or iron*^{III}.

Page 405, line 13: for 1933 read 1923.

Page 295: the journal in reference 2 should read *Ind. Eng. Chem.*

Page 355, title, Summary, first paragraph and under Reagents: for 5-(3-*nitrophenylazo*)*salicylate* read 5-(4-*nitrophenylazo*)*salicylate*.

Page 359, Fig. 5: for 5-(3-*nitrophenylazo*)*salicylate* read 5-(4-*nitrophenylazo*)*salicylate*; also, the nitrophenylazo group should be shown in the 5-*position* and not in the 4-*position*.

Page 363, Zusammenfassung: for 5-(3-*nitrophenylazo*)*salizylsäure* read 5-(4-*nitrophenylazo*)*salizylsäure*.

Page 364, Résumé: for 5-(3-*nitrophénylazo*)*salicylique* read 5-(4-*nitrophénylazo*)*salicylique*.

Page 452, second paragraph of Introduction: the reagent should read *N*-(1-*naphthyl*)*ethylenediamine dihydrochloride*.

Page 457, caption to Fig. 1: the final sentence should read *Reagent solutions contain* $2{\cdot}5 \times 10^{-5}$ *mole of* $Cu(NO_3)_2$ [*or* $CuCl_2$] *and* $8{\cdot}5 \times 10^{-5}$ *mole of di-octen in hexone medium*.

Page 381, line 5: for *stimulate* read *simulate*.

Page 384: the heading on the last column of Table III should refer to the footnote by reading *Corrected*[a].

Page 387, line 8 of Introduction: this should read *complex fluoride ions. All of the fluoride, both free and in the form of tantalum complex, complexes with boron.*

Page 449, Preliminary Communication by F. Vydra and V. Marková: *Received* 13 *February* 1962. *Accepted* 22 *February* 1962.

Page 609: reference 11 should read *Talanta*, 1962, **9**, 581.

Page 813, Fig. 1: higher curve is for *concentrated hydrochloric acid* and lower curve for *constant boiling hydrochloric acid*.

Page 815, line 4 of *Comparison of results between methods and with standards:* for *oxide* read *iodide*.

Page 817, line 2 under Table V: for 057 read 0·057.

Page 835, paper by G. Gopala Rao, P. V. Krishna Rao and K. S. Murty: *Accepted* 1 *June* 1962.

Page 917: this paper is actually *Part II* of the series.

Page 919, last line: for *expression* (1) read *equation* (1).

Page 1060: the second formula should be

